Systematic
Inorganic Chemistry

SYSTEMATIC INORGANIC CHEMISTRY

FROM THE STANDPOINT OF THE PERIODIC LAW

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PREFACE TO FIRST EDITION

This book is intended for students reading for final degree and other advanced examinations, and possessing the amount of information on the properties of the elements and their compounds, and of technical processes, usually covered by the intermediate university courses.

We think that, by omitting the more elementary parts, we shall have brought the systematic aspect of the subject more clearly into prominence. The Periodic Law still affords the most complete method of systematic classification, and our treatment is based upon it—the book being, indeed, an exposition of that law.

The chapters on the Atomic and Molecular Theories, on Oxides and Allied Compounds, and on Oxidation and Reduction, are not intended to be complete accounts of these topics, but rather to recapitulate what the advanced student already knows. We presuppose some acquaintance with the elements of modern physico-chemical theory; and we have not hesitated to draw illustrations, when desirable, from the chemistry of the carbon compounds.

We have made free use of the best modern textbooks and current literature, and desire to acknowledge our indebtedness especially to the works of Dammer, Mendeléeff, Roscoe and Schorlemmer, Ostwald, and Treadwell.

R. M. C.
G. D. L.

PREFACE

TO THE FIFTH EDITION

For this edition the book has been thoroughly revised and much new matter added.

In particular, the notes on the electronic interpretation of valency and molecular structure, formerly placed in an Appendix, are now incorporated in the text. To meet these changes, Chapters I and II have been recast utilizing some material from Chapter XIV. Chapter I contains the older atomic and molecular theories, Mendeléeff's periodic law, and pre-electronic theories of valency. Modern electronic theories appear in Chapter II, and Chapter XIV deals with radioactivity and nuclear transformations. A discussion of oxidation and reduction from the electronic standpoint is given, and the importance of the newer study of crystal structure is shown in the section dealing with the silicates.

Sources of information are indicated by the name of the author (in case of joint-authorship the first name is given) and the year of publication. It is hoped that these will serve as due acknowledgment, and also admit of further reference through the Indexes of *British Chemical Abstracts*, *Chemical Abstracts*, and *Chemisches Zentralblatt*.

I am deeply indebted to the publications of Professor N. V. Sidgwick, and to the Contributors in the *Annual Reports on the Progress of Chemistry*, published by the Chemical Society. I have to thank Professor J. Muir and Dr. M. M.

J. Sutherland, of the Royal Technical College, Glasgow, for helpful discussion, and the assistance of the latter in reading the proofs is gratefully acknowledged.

It is a privilege to offer this Revision as a tribute to the memory of an inspired teacher, Dr. R. M. Caven.

June, 1936.

NOTE TO PRESENT EDITION

The present Edition has given an opportunity to make a few corrections and improvements. Several portions of the text have been re-written in order to include well-established advances.

A. B. C.

March, 1939.

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Atomic Numbers and Atomic Weights of the Elements (1935)

Atomic Number.	Name.	Symbol.	Atomic Weight.
1	Hydrogen	H	1·0078
2	Helium	He	4·002
3	Lithium	Li	6·94
4	Beryllium	Be	9·02
5	Boron	B	10·82
6	Carbon	C	12·003
7	Nitrogen	N	14·008
8	Oxygen	O	16·000
9	Fluorine	F	19·00
10	Neon	Ne	20·18
11	Sodium	Na	22·997
12	Magnesium	Mg	24·32
13	Aluminium	Al	26·97
14	Silicon	Si	28·06
15	Phosphorus	P	31·02
16	Sulphur	S	32·06
17	Chlorine	Cl	35·457
18	Argon	A (Ar)	39·94
19	Potassium	K	39·096
20	Calcium	Ca	40·08
21	Scandium	Sc	45·10
22	Titanium	Ti	47·90
23	Vanadium	V	50·95
24	Chromium	Cr	52·01
25	Manganese	Mn	54·93
26	Iron	Fe	55·84
27	Cobalt	Co	58·95
28	Nickel	Ni	58·69
29	Copper	Cu	63·57
30	Zinc	Zn	65·38
31	Gallium	Ga	69·72
32	Germanium	Ge	72·60
33	Arsenic	As	74·91
34	Selenium	Se	79·2
35	Bromine	Br	79·91
36	Krypton	Kr	83·7
37	Rubidium	Rb	85·45
38	Strontium	Sr	87·63
39	Yttrium	Y	88·93
40	Zirconium	Zr	91·22
41	Columbium (Niobium)	Cb (Nb)	92·91
42	Molybdenum	Mo	96·0

Atomic Number.	Name.	Symbol.	Atomic Weight.
43	Masurium	Ma	—
44	Ruthenium	Ru	101·7
45	Rhodium	Rh	102·9
46	Palladium	Pd	106·7
47	Silver	Ag	107·880
48	Cadmium	Cd	112·41
49	Indium	In	114·8
50	Tin	Sn	118·70
51	Antimony	Sb	121·76
52	Tellurium	Te	127·61
53	Iodine	I	126·92
54	Xenon	Xe	131·3
55	Cæsium	Cs	132·91
56	Barium	Ba	137·36
57	Lanthanum	La	138·90
58	Cerium	Ce	140·13
59	Praseodymium	Pr	140·92
60	Neodymium	Nd	144·27
61	Illinium	Il	—
62	Samarium	Sm	150·43
63	Europium	Eu	152·0
64	Gadolinium	Gd	157·3
65	Terbium	Tb	159·2
66	Dysprosium	Dy	162·46
67	Holmium	Ho	163·5
68	Erbium	Er	167·6
69	Thulium	Tm	169·4
70	Ytterbium (Neoytterbium)	Yb	173·04
71	Lutecium (Cassiopeium)	Lu (Cp)	175·0
72	Hafnium	Hf	178·6
73	Tantalum	Ta	181·5
74	Tungsten (Wolfram)	W	184·0
75	Rhenium	Re	186·31
76	Osmium	Os	191·5
77	Iridium	Ir	193·1
78	Platinum	Pt	195·3
79	Gold	Au	197·2
80	Mercury	Hg	200·61
81	Thallium	Tl	204·39
82	Lead	Pb	207·21
83	Bismuth	Bi	209·00
84	Polonium	Po	—
85	—	—	—
86	Radon (Emanation)	Rd (Em)	222·00
87	—	—	—
88	Radium	Ra	225·97
89	Actinium	Ac	—
90	Thorium	Th	232·12
91	Protoactinium	Pa	230·6
92	Uranium	U	238·14

INORGANIC CHEMISTRY

CHAPTER I

THE ATOMIC AND MOLECULAR THEORIES CLASSIFICATION AND THE PERIODIC LAW

When two or more substances unite together to produce a third substance, as, for example, when copper unites with oxygen to form copper oxide, an examination of the nature and result of the change reveals certain qualitative and quantitative relationships between the interacting substances and the product or products of the reaction.

Qualitatively, adhering to the example stated, and supposing the change completed, the product of the operation is seen to differ in obvious properties, and in its relationships to other substances, from copper, which as a metal has disappeared, and from oxygen, which no longer exists in the system as a gas. Nevertheless, both copper and oxygen are obtainable from the product of their union by suitable processes of analysis.

A change has therefore occurred different from that procurable by a simple process of mixture, and it may be concluded that a more intimate state of union has been entered into. Moreover, the change from metal to oxide is not gradual but sudden, or at any rate takes place in well-defined stages; an intermediate stage consisting in the formation of a lower oxide of copper is possible in the case discussed, but what is true for the final is equally true for the intermediate stage. If the change is incomplete, a part of the copper will be found in the form of oxide, the remainder unchanged.

Material changes, such as that just described, are generally

observed to be accompanied by the evolution or absorption of energy in the form of heat, light, or electricity. When, for instance, copper and oxygen are brought together under conditions in which they combine spontaneously, a considerable amount of heat energy is evolved, so that less energy is present in the system after the change than before.

Quantitative examination of the action reveals regularities of a striking and far-reaching character. The evidence of the balance shows that the actual mass proportions in which the participants of the reaction combine is fixed, as well as the amount of the substance formed, no matter whether the oxide in question is produced directly or by an indirect process, and that from a given mass of the compound the same mass of each of the constituents may always be obtained by analytical processes. These facts depend firstly upon the law of the indestructibility of matter or conservation of mass, established by Lavoisier about 1770, and secondly upon the law of definite or constant proportion which was recognized as the outcome of a controversy between Berthollet and Proust in the years 1801 to 1808.

Law of definite proportion.—*The same compound always contains the same elements combined together in the same definite mass proportion*; or, *the masses of the constituent elements of every compound bear an unalterable ratio to each other, and to the mass of the compound formed.*

In the case under consideration 3·973 parts by weight of copper invariably combine with 1 part of oxygen to form 4·973 parts of black copper oxide.

The evolution of heat energy in such a combination as this is also susceptible of quantitative measurement, and for any particular reaction is constant in amount, the final result being the same in whatever way the reaction is brought about. For instance, when 3·973 gr. of copper combine with 1 gr. of oxygen gas, heat equal to 23·25 K * is evolved.

* K = a large calorie, i.e. the amount of heat required to raise a gramme of water from 0° to 100°.

When two substances combine, more than one product may result. If so, the mass proportions in which combination takes place are simply related, being expressed by such ratios as 1 : 2, 2 : 3, and so forth.

Copper, for example, forms with oxygen a compound containing 7·946 parts of copper to 1 of oxygen, that is, exactly twice the proportion of copper contained in the previous compound.

If in any case a mixture of the two oxides were obtained and analysed, the proportion of copper present might be found to lie anywhere between the two extremes; and so it might appear that the composition of oxide of copper could vary within certain limits. A mistake of this kind was made by Berthollet, who on this account denied the law of definite proportions.

For instance, in the case of tin, two oxides are known in which the proportion of tin to oxygen is

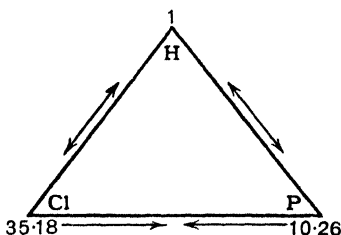
7·44 : 1 and 3·72 : 1 respectively.

If a mixture of these two oxides were analysed the proportion of tin to oxygen would be found to be between 7·44 and 3·72. Proust showed, however, that the variation observed by Berthollet was due to the existence of mixtures in indefinite proportions of two compounds, each of definite composition; and as an outcome of the work of Proust and of Dalton the following law was established:

Law of multiple proportions.—*When the same two elements combine together to form more than one compound, the different masses of one of the elements which unite with a constant mass of the other, bear a simple ratio to one another.*

If an element is known to combine separately with two other elements which also possess power of combination with each other, then further simple mass relationships present themselves. For instance, 1 part of hydrogen is found to combine on the one hand with 35·18 parts of chlorine, and on the other with 10·26 parts of phosphorus. Then it is found that 10·26 parts of phosphorus is the amount which will combine with

35·18 parts of chlorine; so that, considering these quantities as representing amounts of phosphorus and chlorine respectively which are " chemically equivalent " to 1 part of hydrogen, it may be said that amounts of these elements which are chemically equivalent to the same amount of a third element are also chemically equivalent to each other.

This fact may be illustrated by the following diagram:

The third law of chemical combination, of which the above instance is an illustration, may now be stated as follows:

Law of reciprocal proportions.—*The masses of different elements which combine separately with one and the same mass of another element are either the same as, or simple multiples of, the masses of these different elements which combine with each other.*

The law of multiple proportions may also apply to the manner of combination of each pair of elements considered in the statement of the law of reciprocal proportions, as is provided for in it.

The facts of constancy of property and constancy of relative combining mass, which are made manifest by a study of the mutual actions of matter in bulk, form the basis of Dalton's atomic theory. This theory accounts for these facts by the doctrine of the atom; what is true for the bulk is supposed equally true for the ultimate individual particle; union known only in bulk is assumed to consist essentially of union between atoms or discrete individuals, which for a given substance are

all alike and possessed of the same mass. Consequently the mass relationships in which matter combines in bulk represent the mass relationships of the ultimate particles.

The atomic theory of Dalton may thus be stated:

(i) *Every element is made up of homogeneous atoms whose mass is constant.*

(ii) *Chemical compounds are formed by the union of the atoms of different elements in simple numerical proportions.*

Modern knowledge has somewhat modified Dalton's conceptions; to what extent must now be briefly considered.

The atom is known to be a complex structure consisting of a positively charged nucleus surrounded by electrons sufficient in number to maintain the neutrality of the atom as a whole.

Again, the atoms of any one element may not all have the same mass. It was supposed by Crookes that the masses of the atoms of an element might vary within certain limits, and first shown to be true with elements derived from radioactive sources. Indeed the majority of the elements each possess atoms which exhibit the same chemical properties, but whose masses vary (isotopy), the atomic weights derived by chemical methods being mean values.

Further, many compounds are known whose atomic proportions are not numerically " simple ", though they are " integral ", and in no way stand apart from the theory.

The modern atomic theory differs from the atomic theory of the Greeks because it is made contingent on fact, and moreover serves as an instrument of investigation and discovery. It is a valuable working method, and not merely an intellectual hypothesis, like classical atomism. It is well to bear in mind that the atomic theory is based upon the laws of chemical combination, and did not originally stand apart from them; and, further, that the theory does not concern itself with the ultimate nature of matter, still less with metaphysical speculations upon its reality, but with the units of chemical exchange. And, if it is argued that since modern discovery has proved that

these units are not atoms in the etymological sense, therefore the atomic theory is discredited, it may be replied that they are real though divisible, and that discredit only results from pushing the theory beyond the limits of the experimental laws.

The atomic theory, thus experimentally deduced, serves as the basis of modern chemistry, and is therefore a fundamental doctrine second only in importance to that of the conservation of mass, upon which indeed it rests. The development of modern chemistry has been on the lines indicated by the theory, and each extension of chemical knowledge has served to amplify the theory.

An ultimate chemical individual, in the case of a particular substance, is either indivisible in a chemical sense,* that is to say, its division is a practical though not a theoretical impossibility, in which case the substance is an element; or else division is possible, and gives rise to new forms of matter, when the substance is a compound. In a study of the elements, or unresolvable components of matter, the first task demanded by Dalton's atomic theory is the determination of the relative atomic masses which, as has been seen, are proportional to the masses in which the elements combine in bulk.

As a theoretical unit, the relative atomic mass or weight of hydrogen, specifically the lightest known substance, is taken.† If combination always occurred between one atom of each element concerned, the problem of atomic weight determination would be a simple one. The relative atomic weight in any case would be identical with the actual weight or proportion in which the element unites with, or is equivalent to, one part by weight of hydrogen. Dalton, indeed, assumed that the simplest manner of combination was always the real one, and devised arbitrary rules by which the number of atoms

* The degradation of radio-active substances being considered for the time being as outside the limits of chemical change.

† For practical purposes, however, it is more convenient to consider O = 16, so that H = 1·008. The International Committee upon Atomic Weights have decided upon this standard, and it is therefore adopted in the descriptive part of this book.

combining was in any case determined. Such a proceeding was unwarranted, no facts being then available by which true atomic weight values could be arrived at. Hence Dalton's atomic weights were really only chemical equivalents.

An element may indeed possess several simply related combining weights, in the sense of combining with one part by weight of hydrogen or its equivalent, in several proportions. For instance, in the compounds methane, ethylene, and acetylene, carbon possesses the combining weights, 3, 6, and 12 respectively; and in the compounds ammonia, hydrazine, and azoimide, nitrogen possesses respectively the combining weights $4{\cdot}\dot{6}$, 7, and 42. Similarly, carbon in union with oxygen, and many metals in union with oxygen or chlorine, possess more than one combining weight, because they form compounds in which the elements are united together in more than one proportion, according to the law of multiple proportions.

Thus the conclusion is arrived at that a certain number of atoms of one element may unite with a variable whole number of atoms of a second. The fact, therefore, that hydrogen and oxygen unite in approximately the proportions by mass of 1 : 8 gives no information as to the atomic weight of oxygen, which, if water is HO, as Dalton assumed, is 8; if H_2O, 16; if HO_2, 4; and so on. Further evidence is necessary to determine this atomic weight, and this evidence is found in the present and other cases by the consideration of the volume relationships in which gases combine.

That the properties of a gas may be referred to its constitution as a system of separate, mobile particles is readily accepted upon consideration of its properties of limitless expansion, adaptability of form, diffusion, and solution in liquids.

Gay-Lussac's Law that *gases combine with one another in simple proportions by volume*, and the corollary that *the densities of gases are simply related to their combining weights*, led to the hypothesis of an equal number of ultimate particles in equal volumes of gases under similar physical conditions. If these

particles be atoms or ultimate individuals, the facts regarding the volume relations in combination as between hydrogen and chlorine or hydrogen and oxygen lead to the contradictory conclusion that the supposed indivisible atoms of hydrogen and chlorine in the first case and oxygen in the second have suffered division into two parts, since the volume of the resulting gas is in each case twice the volume which would result from pure synthesis of atoms.

Thus, since

1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride, and
2 volumes of hydrogen + 1 volume of oxygen give 2 volumes of steam,

or

1 volume of hydrogen chloride is obtained from half a volume of hydrogen and half a volume of chlorine, and 1 volume of steam from 1 volume of hydrogen and half a volume of oxygen,

it is concluded that

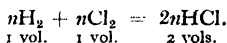
1 compound atom of hydrogen chloride consists of half an atom each of hydrogen and chlorine, and that 1 compound atom of steam consists of 1 atom of hydrogen and half an atom of oxygen.

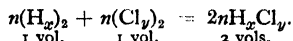
The introduction into the science by Avogadro of the idea of the molecule as a complex particle of a higher order than the atom, composed itself of atoms, alike in the molecule of an element, unlike in that of a compound, resolved this contradiction. The molecules of hydrogen, oxygen, and chlorine do suffer division into two parts, these parts then reuniting to form molecules of compounds. These facts and ideas find expression in **Avogadro's theory,*** which states that *equal volumes of all gases or vapours, simple or compound, contain, under similar conditions of temperature and pressure, equal numbers of molecules.*

* This statement has passed beyond the region of hypothesis, and stands in the same category as the atomic theory. It is not a law, however, not being a summary of experimentally ascertained facts.

This theory is substantiated by the kinetic theory of gases. Granting a fundamental and most probable assumption as to the nature of the motions of gas particles, and the effect of heat upon them, the purely dynamical reasoning of the kinetic theory demonstrates the truth of Avogadro's theory, and therefore of the views of chemical change between gases based on that theory.

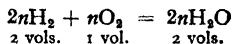
An examination of the phenomena of union between hydrogen and chlorine gases now leads to the conclusion that equal volumes of hydrogen and chlorine, containing the same number of molecules, unite, giving twice that number of molecules of hydrogen chloride; *n* molecules of hydrogen and *n* molecules of chlorine give $2n$ molecules of hydrogen chloride. The constituent atoms of each molecule of hydrogen have undergone separation and union with the atoms resolved from the molecules of chlorine. If now a molecule of hydrogen chloride is formed by the combination of 1 atom of hydrogen and 1 atom of chlorine, the conclusion follows that the molecules of these gases consist each of 2 atoms; thus:

$$\underset{\text{1 vol.}}{nH_2} + \underset{\text{1 vol.}}{nCl_2} = \underset{\text{2 vols.}}{2nHCl}.$$

But the molecule of hydrogen might be H_4, and that of chlorine Cl_2, hydrogen chloride being H_2Cl, a relation satisfying the volumetric data; or, generally, the reaction might be

$$\underset{\text{1 vol.}}{n(H_x)_2} + \underset{\text{1 vol.}}{n(Cl_y)_2} = \underset{\text{2 vols.}}{2nH_xCl_y}.$$

The assumption that a molecule of hydrogen chloride results from the union of 1 atom of each constituent is, however, the simplest, and accords with all known facts. The fact that only one compound of hydrogen and chlorine exists, and the more important fact that either hydrogen or chlorine can only be expelled from hydrogen chloride in one stage, furnish such a strong argument for this assumption as to make it exceedingly probable.* Indeed, if an atom be defined as the smallest

* The argument concerning the manner of displacement of elements from a compound is capable of extension. For instance, the hydrogen can be expelled from

particle which up to the present time has resulted from the disruption of a molecule, then these molecules must at present be considered to contain only 2 atoms, and are therefore written H_2 and Cl_2. The molecule of oxygen is for similar reasons written O_2. Thus the equation

$$\underset{2\ \text{vols.}}{2nH_2} + \underset{1\ \text{vol.}}{nO_2} = \underset{2\ \text{vols.}}{2nH_2O}$$

represents the formation of water, and the formula for a molecule of this substance being H_2O, the atomic weight of oxygen is 16.

METHODS OF ATOMIC WEIGHT DETERMINATION

I. *The Methods of Vapour Density*

It was shown by Gay-Lussac that the combining weights of the simple gases are proportional to their densities; and as a consequence of Avogadro's theory it is further recognized that the molecular weights of all gaseous substances are proportional to their relative densities. If the density of a gaseous compound, referred to hydrogen as unity, be x, the molecular weight of the compound is $2x$, that of hydrogen being 2.

Hence the problem of atomic weight determination resolves itself into ascertaining by analysis, where data are available, the smallest proportion by weight of an element which enters into the composition of a molecular proportion of the gas as indicated by the determination of its vapour density. An approximate value for vapour density is sufficient, accurate knowledge of a molecular weight being derived from analytical data when once the order of its magnitude is determined.

methane in four stages, the carbon in one. Therefore the formula for methane is CH_4, and the atomic weight of carbon 12.

Again, accepting the atomic weights of carbon and oxygen as 12 and 16 respectively, the empirical formula for acetic acid is CH_2O. The oxygen, however, may be expelled in two stages, thio-acetic acid being formed by the substitution of 1 atom of oxygen by sulphur. Therefore the molecular formula is probably $C_2H_4O_2$. And in general—When $\frac{1}{n}$th of the proportion of a constituent element in a chemical compound can be substituted, a molecule of the compound contains at least n atoms of that element.

The molecular weight M of a compound $A_xB_yC_z$ is equal to $(xa + yb + zc)$, where a, b, and c are the atomic weights. The factors x, y, z must be whole numbers. The smallest proportion of an element ever found in a molecular proportion of one of its compounds is considered for the time being as the atomic proportion, and if the number of gasifiable compounds known is large, this value is very probably the atomic weight of the element. An example will make this clear.

Phosphorus forms a number of gasifiable compounds whose vapour densities have been determined, among which are phosphine, liquid hydride of phosphorus, phosphorous chloride, phosphoryl chloride, thio-phosphoryl chloride. A determination of the gas density of phosphine shows the molecular weight to be about 34; and by analysis 33·74 parts by weight of the compound contain 3·0 parts of hydrogen. Therefore the atomic weight of phosphorus cannot be greater than 30·74, though it may be a submultiple of this number. Similarly, the molecular weights and molecular proportions of phosphorus in the other compounds are the following:

	Liquid hydride.	Phosphorous chloride.	Phosphoryl chloride.	Thio-phosphoryl chloride.
Molecular weight ..	65·48	136·28	152·16	168·10
Molecular propn. of P.	61·48	30·74	30·74	30·74

These figures make it probable that 30·74* is the atomic weight of phosphorus, since no molecular proportion of a compound is known to contain less than this amount of the element. At the same time the liquid hydride appears to contain 2 atoms of phosphorus, and to possess the formula P_2H_4.

The method of atomic weight determination discussed above does not require exact values of molecular weights and indeed the value obtained by multiplying the density of the gaseous substance by two is not accurate. Avogadro's theory is subject to the same disability as Boyle's Law, namely, gases are not ideal but have varying compressibilities, hence equal volumes

* Or 30·98 if O = 16 and H = 1·0078.

of gases under similar conditions of temperature and pressure will not contain exactly equal numbers of molecules. These deviations diminish with diminution of pressure and appear to vanish as the pressure approaches zero, so that, if the limiting densities of gases are determined as the pressure tends to zero, the molecular weight values derived therefrom should be more accurate. In practice, the limiting densities are obtained by correcting the normal density values, for the following relation holds:

$$\text{limiting density} = \text{normal density} \times \frac{p_1v_1}{p_0v_0},$$

where p_1v_1 is the value of pv for the gas at one atmosphere pressure, and p_0v_0 the value as p approaches zero.

The value of p_0v_0 may be found by plotting several measurements of pv against p, and extrapolating the curve to $p = 0$.

Or, if the gas does not deviate much from Boyle's Law, the coefficient of compressibility λ, may be used, for when p_1 is one atmosphere, then

$$p_0v_0 = p_1v_1\,(1 + \lambda),$$

the density correction being,

$$\text{limiting density} = \text{normal density}/(1 + \lambda).$$

When measuring the density of nitrous oxide relative to oxygen, Cawood and Patterson (1933) found the following values:

	Normal Density.	$(1 + \lambda)$.	Molecular Weight.
Nitrous oxide	1·9777	1·0071	M
Oxygen	1·42896	1·00094	32

Hence,

$$M = \frac{1{\cdot}9777 \times 1{\cdot}00094}{1{\cdot}42896 \times 1{\cdot}0071} \times 32$$

$$= 44{\cdot}016.$$

Assuming that nitrous oxide is N_2O, the atomic weight of nitrogen (O = 16) is 14·008, in agreement with the accepted value.

II. *The Method of Specific Heat*

A means of fixing the atomic weight, depending on the previous determination of combining weight, and not involving a knowledge of the atomic structure of compounds, is afforded by the application of **Dulong and Petit's law** of atomic heats. In its widest sense the law asserts that *quantities of elements proportional to their atomic weights possess equal capacities for heat*, and fixes this constant heat capacity at 6·4, so that

$$\text{At. wt.} \times \text{sp. ht.} = 6{\cdot}4; \text{ or at. wt.} = \frac{6{\cdot}4}{\text{sp. ht.}}$$

The law thus implies an equal heat capacity for all atoms. It will be seen that in order to fix the atomic heat value so that the atomic weights calculated from it may be of the right order of magnitude, it is necessary for the atomic weight of some one element at least to be accurately established by independent evidence. The convergence of evidence from various sources gradually brought about a settled opinion as to the magnitude of atomic weight values of such well-known elements as copper and iron, and thus it was shown that the atomic weights calculated by Dulong and Petit, although inaccurate owing to faulty data, were of the right order of magnitude.

It was shown by Boltzmann (1871), that the atomic heat at constant volume, C_V, of a monatomic solid element should be equal to 3R, or 5·96 calories, where R is the gas constant. The atomic heat at constant pressure is somewhat greater and is closer to the Dulong-Petit constant, 6·4, which has therefore some fundamental significance.

At ordinary temperature, solid elements, generally metals of atomic weight greater than 30, conform to this law, non-metallic elements of low atomic weight and high melting point being abnormal, although at higher temperatures they tend to approach Dulong and Petit's value.

Experimental determinations of the variation of specific heat with temperature have been carried out by Humpidge in the

case of beryllium, and by H. F. Weber in the cases of boron, carbon, and silicon. The specific heat of beryllium is ·3973 below 50°, increases with rise of temperature, and becomes constant, and equal to about ·62 between 400° and 500°. The rates of variation with temperature of the specific heats of boron and carbon are similar to each other, and the values become constant at about 1000°; the specific heat of boron at this temperature is about ·50, and of carbon ·46. A constant value, ·203, is established for the specific heat of silicon at 200°. The products of these values and the accepted atomic weights of the three elements are approximately 5·5; and thus it is recognized that these elements have distinctly lower atomic heats than the metals. Sulphur and phosphorus also give values somewhat less than 6·4.

On the other hand, if the temperature be lowered, all atomic heat values approach zero at 0° Absolute temperature. Experimentally therefore, the specific heats of all elements increase with rise of temperature, generally rapidly at first, and then more slowly, until a slowly increasing maximum is reached at high temperatures.

These changes cannot be explained on the classical theories which considered the emission or absorption of energy to occur continuously. Explanation of the variation of atomic heat with temperature requires the introduction of Planck's quantum theory according to which the energy changes of vibrating particles, or " resonators ", are discontinuous, occurring in quanta. The value of a quantum ϵ is not fixed, but is proportional to the frequency ν of the vibrating particle, and is defined thus:

$$\epsilon = h\nu,$$

where h is Planck's constant, $6{\cdot}55 \times 10^{-27}$ erg-secs.

Discussion of these theories must be sought in suitable textbooks, but it may be noted that Debye has obtained a mathematical expression for C_v, the atomic heat at constant volume, which reproduces the experimental variations with

great fidelity. In particular he shows that at high temperatures C_V approaches the value of 5·96, but, at extremely low temperatures,

$$C_V = 234 \frac{T^3}{\theta^3}$$

being indeed zero when T is 0° Absolute. Here θ has the dimensions of temperature, and is equal to

$$\frac{Nh\nu_m}{R},$$

where N is Avogadro's constant, h is Planck's constant, R is the gas constant, and ν_m a characteristic vibration frequency which varies from element to element. Consequently θ also varies, being for example, 88 for lead, and 1860 for carbon in the form of diamond. It has thus a high value for elements which depart from the simple Dulong-Petit law at ordinary temperature.

According to Lindemann, the characteristic vibration frequency ν_m, to which θ is related, has a high value when the substance has a high melting point, or a low atomic weight and atomic volume (q.v.). Thus silicon and carbon with high melting-points and low atomic weights do not obey Dulong and Petit's law at ordinary temperatures, whereas the small atomic weight of lithium is compensated by its low melting-point and higher atomic volume, and it obeys the law at ordinary temperatures.

III. *The Method of Isomorphism*

A third aid in fixing the correct multiple of the combining weight of an element which is to be received as its atomic weight is given by the phenomena of isomorphism, or similarity in crystalline form, which were first observed by Mitscherlich. In respect to its application to atomic weight determination, the **law of isomorphism** may be expressed in the following way: *When in a given compound the replacement of one element by another does not alter the crystalline form of*

the compound, the element introduced is chemically analogous to the element replaced, and its compounds will be of the same type.

A practical illustration of the use of the law by Mitscherlich and Berzelius will make clear its mode of application.

Sulphates contain the oxide SO_3, and chromates, being isomorphous with sulphates, must contain the oxide CrO_3 instead of CrO_6 as was previously supposed. Hence chromic oxide must be Cr_2O_3, and not CrO_3. The isomorphism of chromic and ferric salts necessitates the formula Fe_2O_3 for ferric oxide, and consequently FeO for ferrous oxide. But magnesium, zinc, nickel, and cobalt salts are isomorphous with corresponding ferrous compounds; hence their oxides must conform to the type MO instead of MO_2 as previously supposed. The agreement of the atomic weights derived from this type with those indicated by Dulong and Petit's law justified the alterations which were thus made in the atomic weight values.

Another instance of the application of the law is furnished by the case of the element gallium. This metal forms an ammonium alum isomorphous with aluminium ammonium alum $Al_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$. The sulphate of gallium is therefore probably $Ga_2(SO_4)_3$, and the oxide Ga_2O_3, whence, the equivalent being 23, the atomic weight is 69. This value is confirmed by other considerations.

A careful examination of the isomorphism of the salts of the alkali metals has been made by Tutton. Thus the replacement of potassium in potassium sulphate by rubidium and cæsium respectively does not alter the crystalline form of the sulphate, though the thermal and optical properties of the crystals undergo slight changes, generally varying in amount in the same sense as the variation in the atomic weights of the metals. The similarity of crystalline form of the sulphates confirms the chemical relationships of the three metals, and harmonizes therein with the analogies revealed by the study of their chemical behaviour.

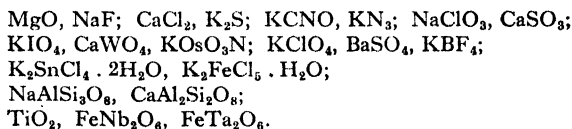
Isomorphous compounds may form mixed crystals, which

are solid solutions, when a solution of a mixture of the salts is allowed to crystallize; or a crystal of a compound may induce crystallization in a supersaturated solution of an isomorphous substance, as in the case of alums.

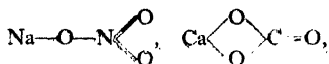
Isomorphism, however, does not imply exact identity of crystalline form, as shown by equality of crystal angles, or of crystallographic axes. The volumes of the structural units must also be similar before mixed crystals are formed. Thus, sodium and potassium chlorides, which are isomorphous, both crystallizing in the regular system, do not form mixed crystals because the volumes of their structural units differ too much.

Equality in the numbers of atoms in the empirical formulæ of two or more compounds points to isomorphism even although the compounds themselves are chemically dissimilar. Thus, sodium nitrate, $NaNO_3$, is isomorphous with calcspar, $CaCO_3$, but from chemical considerations was formerly represented as having a different structure.

Indeed, Mitscherlich originally supposed that isomorphism depended primarily on equal numbers of atoms and similar modes of arrangement, rather than upon their intrinsic chemical nature; and this example lends support to this view. Other groups of dissimilar but isomorphous chemical compounds are:

> MgO, NaF; $CaCl_2$, K_2S; $KCNO$, KN_3; $NaClO_3$, $CaSO_3$;
> KIO_4, $CaWO_4$, $KOsO_3N$; $KClO_4$, $BaSO_4$, KBF_4;
> $K_2SnCl_4 . 2H_2O$, $K_2FeCl_5 . H_2O$;
> $NaAlSi_3O_8$, $CaAl_2Si_2O_8$;
> TiO_2, $FeNb_2O_6$, $FeTa_2O_6$.

Such facts may well give rise to questions concerning the nature of the valency forces concerned and their representation by bonds joining atoms together.

The structures of $NaNO_3$ and $CaCO_3$ were formerly represented thus:

$$Na{-}O{-}N\begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}, \quad Ca\begin{smallmatrix} O \\ O \end{smallmatrix}C{=}O,$$

but these are not in agreement with the isomorphism they exhibit.

A satisfactory solution of these problems will be found in the modern views of atomic structure and valency shortly to be discussed.

IV. *The Mass Spectrograph Method*

This method is dealt with on p. 47, and is valuable for the determination of atomic weights. It is mentioned here because of the independent and confirmatory testimony it gives of the truth of the atomic theory so far as the latter may be developed by chemical methods.

VALENCY

The molecular composition of many gasifiable binary compounds, containing only one atom of one of the constituent elements, shows that a single atom may combine with more than one other atom, a conclusion also to be drawn from the data of the law of multiple proportions.

The following series of gasifiable binary compounds, whose molecular composition may be arrived at by the application of principles studied above, serves as an illustration:

HCl, HBr, H_2O, H_2S, H_3N, H_3P, H_4C, H_4Si, Cl_5P, Cl_6W, F_7I, F_8Os.

From this series it is possible at once to form a conception of valency, or saturation or combining capacity, in the narrower sense, as expressing the largest number of other atoms with which the atom of a given element is known directly to combine.

Thus, for instance, from the above, the valency of sulphur appears to be two, that of nitrogen three, carbon four, phosphorus five, tungsten six, iodine seven, and osmium eight.

No binary compound in which 1 atom of hydrogen combines directly with more than 1 atom of another element is known;* therefore, as regards combining capacity or valency,

* In N_3H only 1 nitrogen atom is attached directly to hydrogen.

hydrogen represents the lower limit, and is designated univalent.

The existence of the gas molecules HF, HCl, HBr, HI shows that the elements fluorine, chlorine, bromine, and iodine may likewise behave as univalent; accordingly these elements are also employed as standards in the determination of valency.

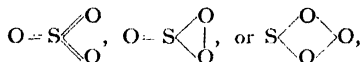
One atom of an element never combines with more than 4 atoms of hydrogen (e.g. CH_4, SiH_4). Higher valency is shown in the halogen compounds, and therefore a distinction must be drawn in practice between hydrogen and halogen valency; for example, the highest hydrogen valency of phosphorus is three, in PH_3, and the highest halogen valency is five, in PF_5 and PCl_5.

The recognition of this distinction raises the question whether valency can be considered to be an inherent property of an atom. It is true that valency is known only in its manifestations, but a consideration of all the types of compound which an element forms, generally leads to a definite conclusion as to the maximum valency which it can exert. The sum of the properties of an element, including the types of its compounds, is shown in the position which it occupies in the periodic system (q.v.). Hence the periodic system may be appealed to for an indication of the potential valency which is an inherent property of an element.

Nevertheless this system sometimes indicates a higher potential valency than is ever realized. Iron, cobalt, and nickel, for instance, are not known to be octivalent, nor is fluorine ever septivalent, as the periodic law indicates. Likewise the bivalency of copper and tervalency of gold are anomalous from this point of view.

In the determination of the valency of a given element it should be remembered that the only direct and rigorous experimental evidence is afforded by a knowledge of the molecular weight and composition of a gasifiable compound containing 1 atom of the element under discussion united to standard univalent atoms. For instance, no indisputable

conclusion as to the valency of sulphur can be drawn from the molecular weight and atomic composition of SO_3, the constitution of which may be represented in three ways,

$$O{=}S\begin{matrix}{\not\!/}O\\ \diagdown\!\!\diagdown O\end{matrix},\quad O{=}S\begin{matrix}/O\\ \ \ \vert\\ \diagdown O\end{matrix},\quad \text{or}\quad S\begin{matrix}/O\diagdown\\ \\ \diagdown O/\end{matrix}O,$$

in which sulphur is respectively sexi-, quadri-, and bivalent. The chemical behaviour of the compound, however, makes it unlikely that it contains a chain of oxygen atoms; hence the conclusion that in SO_3 sulphur is sexivalent, a conclusion which is fully upheld by the periodic law, and has been confirmed by the preparation of sulphur hexafluoride, SF_6.

A knowledge of the atomic weight of calcium, again, leads to the formulæ $(CaO)_n$ and $(CaCl_2)_n$ for the oxide and chloride respectively; but whatever may be the real molecular magnitudes of these compounds, or whether definite molecules exist at all, their atomic composition is accurately represented by the simplest formulæ CaO and $CaCl_2$. Calcium is accordingly regarded as bivalent; and here also the periodic law affords testimony to the correctness of this conclusion.

Some complication of the simple facts of valency arises from the display by many elements of varying valency; for example, by tin in $SnCl_2$ and $SnCl_4$, by iron in $FeCl_2$ and $FeCl_3$, by phosphorus in PCl_3 and PCl_5, and by tungsten in WCl_4, WCl_5, and WCl_6. A number of elements exhibit valencies which, increasing or diminishing by two, are always either odd or even, and formerly it was thought that a regularity of this kind existed which might be called a law. Such is not the case, numerous examples of increase or decrease by single units being known. The group valencies indicated by the periodic law are, however, seldom if ever exceeded, and these therefore indicate the maximum values for the various groups of elements. It must nevertheless be remembered that the manifestation of valency is contingent upon chemical combination; whenever union occurs, valency must come into operation as a measure of its extent. Active valency is not,

therefore, a constant property like atomic mass; indeed it has been well compared with the force of friction, which is only called into play by external causes, and may vary from zero to a certain maximum.

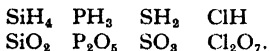
The existence of the so-called "molecular compounds" raises a difficult question. This term was formerly applied to substances whose structure was inexplicable on the ordinary laws of fixed valency; salts containing water of crystallization, double salts such as the alums, and complex salts such as ferrocyanides and platinichlorides serve as illustrations.

The special application of the term "molecular compound" implies a difference in the nature of the union of the constituent atoms from that obtaining in an ordinary compound. This distinction is unwarranted by the facts. Salts like the chloroplatinates—or platinichlorides—and the ferro- and ferricyanides exist in solution, and therefore contain complex ions, so that the mode of union within them must be considered to be atomic; and from these compounds to the alums and other double salts, which are more or less decomposed by water, all stages of stability exist. Moreover, molecular compounds may enter into reactions of double decomposition or metathesis; thus triethylammonium tribromide, which might be considered a molecular compound of triethylamine and bromine, reacts with potassium iodide, as shown by the equation $(C_2H_5)_3NBr_3 + 3KI = (C_2H_5)_3NI_3 + 3KBr$; and the five molecules of water of crystallization in $CuSO_4, 5H_2O$, are successively replaceable by ammonia, with the ultimate formation of $CuSO_4, 5NH_3$. Analogous phenomena are abundantly provided by the "ammines" and allied compounds of the metals of the eighth group of the periodic system, and the chemical changes and transpositions which these substances undergo are characteristic of normal chemical compounds. Many molecules which are generally considered saturated, e.g. $C_2H_4O_2$ and HF, and even H_2O, are known to polymerize; $(C_2H_4O_2)_2$ and $(HF)_2$, indeed, can exist in the gaseous state.

There is no intrinsic difference, therefore, between the

ordinary and the molecular compound, except that the latter generally undergoes dissociation more readily than the former. The development of higher valencies must consequently be assumed in order to account for these compounds; and the question arises as to what further justification there is for this assumption.

Now it may be observed that the sum of the maximum hydrogen and oxygen valencies of elements in certain groups of the periodic system is equal to eight. The following series of compounds illustrates this fact:

$$\begin{matrix} SiH_4 & PH_3 & SH_2 & ClH \\ SiO_2 & P_2O_5 & SO_3 & Cl_2O_7. \end{matrix}$$

According to Abegg,* every element possesses a maximum valency of eight, made up of positive and negative components, or normal and contra-valencies. These are composed as follows, taking a single series for illustration:

	Na	Mg	Al	Si	P	S	Cl
Normal valences ..	+ 1	+ 2	+ 3	± 4	− 3	− 2	− 1
Contra-valencies ..	− 7	− 6	− 5		+ 5	+ 6	+ 7

The contra-valencies are latent in the first three elements of the series; and the quality of the valency manifested by a particular atom depends on the character of the element or group with which it is associated. Thus chlorine manifests a single negative valency towards hydrogen or metals, and a maximum positive valency of seven towards oxygen.

The relative strengths of the two kinds of valency depend upon the chemical nature of the atom itself. Thus the alkali metals are too electropositive to show negative valencies, and fluorine was supposed to be too negative to exhibit positive valencies, although recently oxides of fluorine have been obtained.

We have seen that atoms possess mass, which, so far as our observations go, remains unchanged in chemical reactions. These reactions, however, disclose the fact that atoms vary

* *Zeitschr. anorg. Chem.* (1904), **39**, 330.

in their capacity to combine with a standard atom. They possess valency, which is not always shown to the full extent possible (maximum valency), but for an atom in combination may have a lesser value, its active valency (or valence). Hence the combining or equivalent weights ascertained from matter in bulk are not always identical with the atomic weights of the atoms concerned. For the simple binary compounds considered above, the reciprocal variation of valency and atomic weight may be summarized thus:

$$\text{valency} = \frac{\text{atomic weight}}{\text{equivalent weight}}.$$

Here, however, the discussion of valency from the older point of view may cease, so as to give place, in the succeeding chapter, to modern conceptions which have revolutionized chemical science, and thrown much light on perplexing problems.

CLASSIFICATION AND THE PERIODIC LAW

The vast mass of experimental data of chemistry only becomes systematic when the elements and their compounds are classified. The nature and aim of classification have been set forth by Huxley in the following words:

" By the classification of any series of objects is meant the actual or ideal arrangement together of those which are alike, and the separation of those which are unlike; the purpose of this arrangement being primarily to disclose the correlations, or laws of union, of properties or circumstances, and secondarily, to facilitate the operations of the mind in clearly receiving and retaining in the memory the characteristics of the objects in question."

The establishment of an inductive law in the experimental sciences involves the following sequence of logical operations:

I. Induction.
II. Verification.
III. Deduction (or Discovery).

By the inductive process the law receives its statement, which is an expression of the common features presented by the observed facts; in the process of verification it must be shown that the law is capable of embracing within its scope other facts as they become known; and by the third or deductive process the availability of the law as an instrument of discovery is tested, and thus new facts or relationships of facts are discovered.

The rise and development of the periodic law as an instrument for the systematic study of the elements, as it is traced in the sequel, will be seen to correspond with and fulfil each of these requirements.

Before proceeding to the exposition of the law, it may, however, be well to glance briefly at some earlier attempts at classification of the elements. Of these the most important was the electro-chemical classification of Berzelius. According to this chemist every atom was the bearer of fixed electrical charges, both positive and negative, and, as these differed in relative magnitude, displayed either a positive or negative electrical " unipolarity "; metallic atoms bore an excess of positive, non-metallic atoms an excess of negative electricity. Combination between atoms was resultant upon the partial satisfaction of their respective charges, the electrical character of the resulting product depending upon the nature of the unsatisfied residue. Thus, in potassium oxide, the positive charge of the potassium not being fully satisfied by the negative charge of the oxygen, a balance of positive charge remained; whilst in sulphur trioxide a balance of negative electricity was present. Combination could therefore ensue between these oxides, yielding potassium sulphate, which still bore a positive residue and was therefore able to unite with aluminium sulphate, which bore a negative charge, to form alum. Union would thus occur in the first instance between atoms, then between binary compounds, and so forth. Berzelius was able to classify the elements in a series in which the gradation with respect to electric character was from posi-

tive to negative, which is equivalent to a transition from metal to non-metal; and the electrical method of union, related to this classification, formed the basis of the dualistic theory of chemical compounds, which for some time held the field.

It will be perceived that the electro-chemical views of Berzelius are the historical predecessors of our modern doctrine of ionic dissociation, according to which a dilute solution of an electrolyte (an acid, base, or salt) contains ions which are the bearers of positive or negative charges. Thus potassium chloride is regarded as existing in dilute aqueous solution in the state of dissociated ions $\overset{+}{K}$ and $\overset{-}{Cl}$, potassium sulphate in the state of ions $2\overset{+}{K}$ and $\overset{-}{SO_4}$, and so forth.

The value of the electro-chemical behaviour and its correlated properties in the study of the chemical character of an element will again be referred to in discussing the periodic variation of the chemical properties of the elements.

Regularities between the atomic weights of the elements were remarked prior to the general statement based on them by Mendeléeff. Döbereiner, for instance, pointed out that the atomic weights of allied elements were either very nearly equal, or separated by regular intervals. Thus iron, cobalt, and nickel formed a triad of elements with nearly equal atomic weights, and lithium, sodium, and potassium a triad whose atomic weight differences Na — Li and K — Na were approximately equal to 16.

The first attempt at a complete classification based on atomic weights was made in 1864 by Newlands, who enunciated the principle of periodicity in his " law of octaves ". By arranging the elements in the order of their atomic weights, he was able to demonstrate the general validity of his statement that " the eighth element, starting from a given element, is a kind of repetition of the first, like the eighth note in an octave of music ".

The periodic law,* however, first received its full statement, in 1869, by Mendeléeff, and it may be expressed as follows: " *The physical and chemical properties of the elements and their compounds are periodic functions of the atomic weights* "; or, " *If the elements are arranged in order of increasing atomic weight, their properties vary in a definite manner from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series* ".

This fundamental proposition serves as the basis of modern classification. In 1870 Lothar Meyer also drew attention to the periodic relationship between certain physical properties of the elements and their atomic weights.

Excluding hydrogen, for which there is no known analogue, and leaving out of consideration for the present the inert gaseous elements, lithium is the starting-point of the following series of seven elements:

Li Be B C N O F,

in which the change of chemical character is from metallic (positive) to non-metallic (negative). Following fluorine is sodium, the analogue or " octave " of lithium, and forming the starting-point of the series or period,

Na Mg Al Si P S Cl,

each member of which is the analogue of the correspondingly situated element of the first period.

From potassium, which follows chlorine, the analogue rubidium is not reached until a longer period of seventeen elements has been traversed,

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Cu	Zn	Ga	Ge	As	Se	Br			
Rb.									

The set of three elements, Fe, Co, and Ni, links the first seven elements with the last seven, and these two series contain, in

* Like the doctrine of valency, the periodic law has to be readjusted to the new knowledge regarding the atoms of matter. The fundamental property of an element is not its atomic weight, but its atomic number (q.v.); the statement of the periodic law gains accuracy by substituting this latter idea for the former. Nevertheless, it is convenient for the present to leave the definition in the old form.

corresponding positions, as shown, elements which are allied to one another, and to the corresponding members of the first or short periods.

The second long period is complete, including the recently discovered analogue to manganese, and runs:

Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd
Ag	Cd	In	Sn	Sb	Te	I.			

The third long period contains 31 elements, of which one, Re, is an analogue of manganese. Another, Po, is a radioactive element, and one, eka-iodine is still unknown. Included also are 14 rare earth elements whose relationship to lanthanum and hafnium will be discussed later. Omitting the rare earth elements, the period comprises·

Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt
Au	Hg	Tl	Pb	Bi	Po	—			

The fourth long period is incomplete, the only members known being:

Eka-Cs	Ra	Ac	Th	Pa	U

Placing hydrogen alone as series one, and dividing the long periods into two series comprising the first seven and last seven members, the three central members being omitted, the elements become arranged in seven groups, each group after series three containing two sets of elements which form sub-groups, A of the elements of even series, B of uneven series. The transitional triads of the long periods then fall into Group VIII, while the inert gases now form Group O. (See diagram, p. 28.)

The allocation of the members of the two short periods into sub-groups A and B is somewhat arbitrary, on account of the fact that these elements display many anomalous relationships to their group successors, just as do the first members of homologous series in carbon compounds. They summarize the properties of the group, however, and are called by Mendeléeff " typical elements ". In referring them to sub-groups, it is

TABLE I

Groups	O	I		II		III		IV		V		VI		VII		VIII
Sub-Groups		A	B	A	B	A	B	A	B	A	B	A	B	A	B	
Series 1			Increase in acid-producing properties →													
" 2	He	Li		Be		B		C		N		O		F		
" 3	Ne	Na		Mg		Al		Si		P		S		Cl		
" 4	A	K		Ca		Sc		Ti		V		Cr		Mn		Fe Co Ni
" 5			Cu		Zn		Ga		Ge		As		Se		Br	
" 6	Kr	Rb		Sr		Y		Zr		Cb		Mo		Ma		Ru Rh Pd
" 7			Ag		Cd		In		Sn		Sb		Te		I	
" 8	Xe	Cs		Ba		La and 14 Rare Earth Elements										
								Hf		Ta		W		Re		Os Ir Pt
" 9			Au		Hg		Tl		Pb		Bi		Po		–	
" 10	Nt	–		Ra		Ac		Th		Pa		U				

↓ Increase in base-producing properties

perhaps best to be guided by the natural relationships; thus it is more reasonable to refer sodium to sub-group A containing the alkali metals, than to sub-group B; though chlorine is evidently to be classed with bromine and iodine in the latter sub-group; and, in general, relationship to the elements of sub-group B becomes closer towards the end of each short period.

In order that the law may be fully established, it is necessary not only that the elements shall fall into groups, but also that the series when complete shall not be interfered with; for instance, no element can be discovered which may be interposed between boron and carbon without invalidating the law. It is further necessary that the nature of the change of property in passing from member to member shall be uniform throughout the series.

The atomic-weight differences in a group are remarkably constant. In the first two periods this difference is approximately 16, as between Na and Li, S and O, Cl and F. With the elements of higher atomic weight the difference is approximately 46, as between Rb and K, Sr and Ca, Sb and As.

It will now be shown how the periodicity is illustrated by the physical properties of the elements, and later in what manner the chemical characters vary.

PHYSICAL PROPERTIES

Density.—The densities of the elements in the solid state vary periodically with the atomic weights, as is shown by the following series:

Na	Mg	Al	Si	P	S	Cl*			
·97	1·75	2·67	2·49	1·82 to 2·34	1·91 to 2·07	1·33			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
·87	1·55	2·5(?)	4·87	5·5	6·92	7·42	7·8	8·5	8·8
Cu	Zn	Ga	Ge	As	Se	Br			
8·93	7·15	5·96	5·47	5·4 to 5·9	4·26 to 4·8	2·97*			

* Densities in liquid state.

It will be noticed that the density varies in a regular manner from member to member of the series, reaching a maximum in the central members; it also increases with increase of atomic weight in a group.

Atomic Volume.—A more comparable magnitude than the density is the atomic volume; this is the ratio of the atomic weight to the density, and is denoted by the symbol V, or A V. This value cannot be expressed absolutely, the actual figures representing the volume in cubic centimetres of an atomic proportion in grammes (the gramme-atom).

The variation in this magnitude is shown at a glance by Lothar Meyer's curve of atomic volumes, in which atomic weights are plotted as abscissæ and atomic volumes as ordinates (see diagram opposite). The members of each period occupy successive positions on the curve, and those of each group occupy similar positions. In the first portion of the curve, containing elements of lowest atomic weight, an anomaly occurs in the relative positions of helium and lithium. According to Onnes,* the density of liquid helium is only 0·15; hence its atomic volume is 26·6, whilst that of hydrogen is 1·44, and that of lithium 13. Thus the curve, ascending steeply from hydrogen to helium, descends again through lithium to beryllium; and so, unlike the other alkali metals, lithium does not occupy an apex. This is another example of anomalies presented by so-called " typical " elements. Certain portions of the curve are incomplete owing to uncertainty of data concerning the metals of the rare earths, and also on account of undiscovered elements.

It will be noticed that the elements of the alkalis occupy the maximum points, the central elements—in the long periods those of the transitional triads—occurring at the minima.

The manner of variation of atomic volume with rise of atomic weight in a group is shown by the line joining the members of a group on the successive curves.

In some cases the atomic volume increases with increase in

* *Proc. K. Akad. Wetensch. Amsterdam* (1908), **10**, 744; **11**, 168.

atomic weight, as in the phosphorus group, but particularly in the group of alkali metals. In the halogen family the atomic volume is constant, and also in the triads of Group VIII.

According to Mendeléeff, the relative magnitudes of the atomic volumes are connected with the chemical activity of the elements, since they roughly measure the size of the inter-atomic spaces, or " porosity " of structure. An element of high atomic volume, or loose texture, such as an alkali metal, may be expected to display greater chemical activity than one of low atomic volume, or dense texture, such as a member of Group VIII.

The quotient molecular weight divided by density gives the *molecular volume* (MV) of a compound, a value which is not strictly the sum of the constituent atomic volumes, the defection being due to atomic arrangement and methods of linking. The problem is important in connection with the newer knowledge of crystal and molecular structure. Ionized salts possess lower, and non-ionized compounds higher, molecular volumes, e.g. NaCl, 37·5; $SiCl_4$, 102·5; both at the melting-point. Nevertheless, periodicity in molecular volume occurs with increase of atomic weight, as with the solid alkali chlorides (Fajans and Grimm, 1920), and the hydrides of Group VI at their boiling points (Pearson and Robinson, 1934):

LiCl	NaCl	KCl	RbCl	CsCl
20·5	27·05	37·52	43·21	42·34

OH_2	SH_2	SeH_2	TeH_2
18·81	35·25	40·54	49·06

A similar periodicity occurs along any period thus:

SiH_4	PH_3	SH_2	ClH	A
50·55	44·50	35·25	29·64	28·5.

The Parachor.—From measurements of the densities of liquids at their boiling points (corresponding temperatures), Kopp stated that the molecular volumes of liquids were the sum of the constituent atomic volumes. The law is approxi-

mate only, since different liquids have different internal pressures or molecular attractions. The surface tension, however, is the outward manifestation of these internal pressures. Using the expression

$$\frac{M}{(D - d)}\gamma^{\frac{1}{4}} = P,$$

Sugden obtained values for the parachor, P. Here M is the molecular weight and D the density of the liquid, d is the vapour density and is small compared with D, γ is the surface tension.

The expression is independent of temperature over a wide range, and is a measure of the molecular volumes of liquids at temperatures when their surface tensions are equal. From the molecular values the atomic parachors may be deduced, and are found to be additive. It is also possible to distinguish the types of linkage present in the molecule. Hence parachor measurements are of great importance in determining molecular structure. They show periodicity with increase of atomic number in a group thus:

O	S	Se	Te
20·0	48·2	61·0	80·0

and in series, thus:

Si	P	S	Cl	A
28·4	39·2	48·2	54·3	54·0

Vibration Frequencies.—The vibration frequencies, v, characteristic of atoms in the solid state (*vide* atomic heats) also vary periodically, and when plotted against atomic weights, give a curve similar to Lothar Meyer's atomic volume curve, the peaks and hollows of the latter being reversed, as befits the reciprocal relationship of the two quantities. The following are values of v for the alkali metals:

Li	Na	K	Rb	Cs
10·0	3·96	2·3	1·45	0·95 × 10^{-12}.

Melting-point.—The melting-points of the elements also vary periodically with the atomic weights. According to Linde-

mann, rise of temperature increases the amplitude of atomic vibrations, collisions occur, and the structure of the solid is destroyed as the substance melts.

Elements at or immediately preceding minima in the atomic-volume curve have high melting-points, e.g. B, C, Si, the metals of Group VIII, which are at minima, and Ti, Mo, Cr, which immediately precede minima.

Elements immediately following minima on ascending curves have low melting-points and relatively great volatility, such as the elements P, S, Cl, Ga, As, Se, Br, Sn, Sb, Te, I in successive sections of the curve. Here again it is noticed that the "typical" elements of low atomic weight are anomalous.

In general, increase in fusibility coincides with rise of atomic volume, and vice versa. Nevertheless the apices of the curves are occupied, not by the halogens or the inert gases, but by the less fusible alkali metals, which commence the periods.

Other Physical Properties.—Many other physical properties, so far as data permit, have been shown to vary periodically with atomic weight. Some of these will be briefly mentioned.

Malleability.—Only elements at or immediately following a maximum or minimum point are malleable, e.g.

Li, Be; Na, Mg at maxima,
Fe, Co, Ni, Cu, Zn } at minima.
Rh, Pd, Ag, Cd }

Brittle, heavy metals occur just before minimum points. Examples of these are:

V, Cr, Mn; Mo, Ru; Os, Ir.

The malleable metals are also the most ductile.

Coefficient of Expansion.—The researches of Fizeau tend to show that volatile elements on ascending curves have larger coefficients of expansion between 0° and 100° than difficultly fusible metals at minimum points.

Atomic Refraction, according to Gladstone, Landolt, and others, varies from a minimum at Group I to a maximum at Group IV.

Colours of Salts.—Bayley has pointed out that colourless acids only form coloured salts with metals at or near minimum atomic-volume points, as may be readily perceived by reference to metals such as Mn, Fe, Co, Ni, Cu, Au, Pt.

Conductivity for Heat and Electricity.—Copper, silver, and gold, the best conductors, occur at transition points between difficultly and easily fusible metals. Thus:

Fe Co Ni	Cu	Zn Ga
Ru Rh Pd	Ag	Cd In
Os Ir Pt	Au	Hg Tl.

Of similarly situated elements, those of higher are not generally such good conductors as those of lower atomic weight.

Chemical Properties.—A detailed consideration of the periodic variation of chemical properties will be made later in the light of the newer theories of atomic structure. Meanwhile, it will suffice to indicate briefly the nature of these variations.

Mendeléeff's classification focusses attention on the periodic nature of valency. The following series of representative oxides and hydrides illustrates this.

I	II	III	IV	V	VI	VII
Li_2O	CaO	B_2O_3	CO_2	N_2O_5	SO_3	Cl_2O_7.
LiH	CaH_2	$B(CH_3)_3$	CH_4	NH_3	OH_2	FH.

Passing from Group I to Group VII, the maximum valency towards oxygen changes from one to seven; concurrently, the oxides show increasing acidic character.

In the hydrogen series of compounds, where $B(CH_3)_3$ represents the unknown BH_3, the valency reaches a maximum of four in Group IV, and falls to one in Group VII. The chemical character of the hydrides varies accordingly. Thus, LiH is a salt, CH_4 a neutral compound, and FH an acid.

In general, therefore, the electropositive character decreases along a series.

An increase of electropositive character is developed on passing downward through the elements in a group, though

exceptions occur here. Hence, the oxides become more basic, or alternatively, less acidic in character. In accordance with these changes, the chemical nature of other compounds also alters, though considerable resemblance is to be expected in similar compounds of elements in the same Group.

PRACTICAL APPLICATIONS OF THE PERIODIC LAW

To be a valid natural law the periodic law must operate as an instrument both of control of present knowledge and of discovery of new facts. From its successful application in both these ways this law derives its most valuable support.

It has been practically applied in two main directions: firstly to the correction of atomic weight values, and secondly to the description of the properties of unknown elements. Atomic weight corrections, instigated by the law, have been of two kinds: (*a*) small corrections affecting the position of an element in series, and (*b*) the determination of the correct multiple of the combining weight of an element, when this is otherwise doubtful. To case (*a*) may be referred the correction of the atomic weight of cæsium determined by Bunsen as 123·4. If this value is accepted, the difference Cs − Rb = 37·95, whereas in greater likelihood it should approximate to Rb − K = 45·35. Redetermination with larger quantities of material gave Cs = 132·81 and Cs − Rb = 47·36, which is in accordance with the law.

The second application (*b*) of the law to atomic-weight determination may be illustrated by the cases of indium, beryllium, and uranium. The chemical equivalent of indium is 38·27.* If the oxide be InO, as was formerly thought, the atomic weight is 76·54. This value places the metal between arsenic and selenium, a position inconsistent with its chemical properties. If, however, the oxide be In_2O_3, the atomic weight becomes 114·8, and the element is placed between cadmium and tin in Group III, along with the analogous metal thallium.

* O = 16.

This change, suggested by Lothar Meyer, was warranted by Bunsen's determination of the specific heat as 0·057, whence

$$In = \frac{6 \cdot 4}{\cdot 057} = 112 \cdot 3.$$

The equivalent weight of beryllium is 4·55. From the isomorphism of the oxide and sulphate with the corresponding aluminium compounds, Nilson and Pettersson attributed the atomic weight 13·65 to this element, the oxide being Be_2O_3; and this value was confirmed by their determination of the specific heat as 0·4079. Beryllium thus falls into an extremely unlikely position between carbon and nitrogen. In spite of the above facts, Mendeléeff considered 9 the correct value for the atomic weight, and placed the metal in Group II. Brauner suggested that the specific heat might vary with temperature, and Humpidge found that between 400° and 500° this value becomes constant and equal to 0·62, thus giving an atomic weight approximating to 9. Moreover, Carnelley pointed out that the melting-point of the chloride, about 600°, does not agree well with the formula $BeCl_3$, the analogously constituted chlorides BCl_3 and $AlCl_3$ possessing far lower melting-points. Finally Nilson and Pettersson succeeded in vaporizing the chloride and ascertaining its molecular weight, whence Be = 9·02, a value consistent with the periodic law.

The atomic weight formerly assigned to uranium was approximately either 60 or 120. Mendeléeff showed that these values did not place uranium in a probable position in the classification, and preferred the value 240, regarding uranium as the heaviest analogue of chromium, the highest oxide being acidic, but less strongly so than chromic anhydride, and forming uranates analogous to the chromates. Further, the highest chloride resembles $MoCl_4$ in volatility. Determinations of the vapour densities of the chloride and bromide by Zimmermann confirmed Mendeléeff's value.

The second application of the periodic law, to the description

of the properties of hitherto unknown elements, affords perhaps the best test of the value of the law. The possibility of such a prediction depends upon the principle that the properties of an element are the mean of those of its atomic analogues. The atomic analogues are those elements immediately preceding and succeeding an element in series and group. Thus the analogues of phosphorus are silicon and sulphur in series, and nitrogen and arsenic in group. The atomic weight, 30·98, is nearly the mean of those of silicon and sulphur. The hydrogen valency is three, that of silicon being four, and of sulphur two. Phosphorus is intermediate in chemical respects between nitrogen and arsenic. It is more positive than nitrogen and less so than arsenic; hence its hydride is but feebly basic, its pentoxide is acidic but less so than that of nitrogen, its chlorides are more stable than nitrogen chloride but are more readily decomposed by water than arsenic chloride.

When Mendeléeff first put forward the periodic classification he sketched the properties of three elements, which if discovered would fill blank spaces then existing in the table. These elements, now known as gallium, scandium, and germanium, he named respectively * eka-aluminium, eka-boron, and eka-silicon, from their analogy with these three known elements. A comparison of the predicted with the actual properties of these elements is interesting.

Eka-aluminium, following zinc in series, and placed between aluminium and indium in group, would be a metal of atomic weight = 69, of low melting-point, and density = 5·9. It would not readily be acted on by air, and would dissolve in acids and alkalis. It would form a potassium alum, and its oxide and chloride would be El_2O_3 and El_2Cl_6 respectively. Gallium, discovered in 1875 by de Boisbaudran, has an atomic weight of 69·72, fuses at 30·15°, and has a density of 5·93. It is not volatile, and is only superficially oxidized in air at a red heat. It decomposes water at high temperatures, and is soluble in hot hydrochloric acid and potassium hydroxide. It

* The prefix eka = *one* in Sanskrit.

forms well-defined alums, and its oxide and chloride are Ga_2O_3 and Ga_2Cl_6 or $GaCl_3$.

Eka-boron would be related to aluminium in the same way as calcium is to magnesium. Its atomic weight would lie between 43 and 46. The oxide Eb_2O_3, density 3·5, would be soluble in acids, but, being more basic than Al_2O_3, would not be soluble in caustic alkalis. Its salts would be colourless and give gelatinous precipitates with alkalis, alkali carbonates, and phosphates. The sulphate would form double salts, probably not isomorphous with the alums. The chloride would be less volatile than $AlCl_3$.

The properties of scandium, discovered by Nilson, fully correspond. The element has the atomic weight 45·1. Its oxide Sc_2O_3, of density 3·8, is soluble in strong acids, but not in alkalis. Solutions of the salts give gelatinous precipitates with sodium hydroxide, carbonate, and phosphate. The sulphate forms a double salt $3K_2SO_4$, $Sc_2(SO_4)_3$ which is not an alum. The chloride $ScCl_3$ breaks up when heated in the air, producing a basic chloride and HCl.

Eka-silicon, lying between silicon and tin, would be related to titanium as zinc is to calcium. Its atomic weight would be about 70. It would be a grey, difficultly fusible metal, obtained by reduction of the oxide with sodium or carbon, and would be scarcely acted on by acids, but readily by alkalis. The oxide EsO_2 would be less basic than titanium dioxide and more so than silicon dioxide. The fluoride would not be gaseous, and would give rise to double fluorides M_2EsF_6, isomorphous with silicifluorides. The chloride would be a liquid boiling at about 100°. The properties of germanium, discovered by Winkler, fully confirm those predicted. The atomic weight is 72·6, and the metal is obtained by reduction of the oxide by carbon or hydrogen; germanifluorides isomorphous with silicifluorides may be obtained. The chloride $GeCl_4$ is a liquid, boiling at 86°.

These facts sufficiently vindicate the periodic law as an instrument of discovery. In astronomy the discovery of new planets,

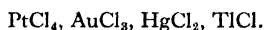
whose existence has previously been foretold by mathematical calculations, has always been considered as a powerful proof of the correctness of the theories on which such calculations are based. A similar conclusion may be drawn in the case of the periodic law.

OBJECTIONS TO THE PERIODIC CLASSIFICATION

The most recent determinations of the atomic weight of tellurium confirm the position of that element as following and not preceding iodine in series; the atomic weight of argon places that element between potassium and calcium, and the atomic weights of nickel and cobalt reverse the order required by the properties of these elements. It is unlikely that the accepted atomic-weight values of the above elements will undergo much alteration, and these discrepancies would appear, therefore, to constitute a serious objection to the periodic law; but, as will be seen in the sequel, atomic numbers rather than atomic weights are the real criterion of the order of sequence of the elements, and atomic numbers in all cases confirm the order required by chemical properties. Moreover, this difficulty has now been completely removed by the discovery that the fractional atomic weights which many of the elements possess represent an average derived from the admixture of two or more isotopes (q.v.) of different integral atomic weights, but inseparable by chemical means.

A further objection is that, apart from small discrepancies, the arrangement of the elements according to their atomic weights is sometimes in opposition to that which would be made in a classification according to properties. Thus the sub-group copper, silver, gold, displays scarcely any likeness to that of the alkali metals; and even when, as in the case of silver, the type of compounds formed is similar, there is wide divergence in the properties both of the metals and their compounds. For example, Ag_2O and Li_2O, $AgCl$ and $NaCl$, differ greatly in properties. It is, however, in Groups I and

VII that the provisions of the periodic law would suggest the greatest dissimilarity between the sub-groups. Copper, silver, and gold approximate in properties to their neighbours in the eighth group, nickel, palladium, and platinum, so that sometimes they have been considered to belong properly to this group. The absence of uniformity of type in the group is, however, anomalous. The tervalency of gold, which appears most unaccountable, enables this element, however, to form one of the following series of chlorides:

$$PtCl_4, AuCl_3, HgCl_2, TlCl.$$

Bivalent iron and manganese in many respects resemble in their compounds the metals of Group II, especially magnesium. Tervalent iron, manganese, and chromium similarly resemble aluminium and the Group III metals. Sexivalent manganese and iron are allied, in manganates and ferrates, to the sulphur group. Manifestly, it would not be permissible to place an element like iron in more than one group. The difficulty may, however, in great measure be overcome in view of the circumstance that the group type is usually best revealed in the compounds of highest valency; thus in Group VII the permanganates ally manganese with the halogens. When, as in the metals named, an element displays several valencies, it is to be expected that the properties of the compounds of types corresponding with these valencies will be similar to those of other compounds of the same type.

In several cases the periodic classification separates, into different groups, elements which show chemical similarities; and this objection has some weight. As examples, Cu and Hg, Ba and Pb, Ag and Tl, may be given. Relationships between these three pairs of metals is shown by reason of isomorphism and solubility of certain salts; but it is open to question whether their differences are not greater than their resemblances. The metals copper and mercury show great contrast in physical properties; copper has a high melting-point, while mercury forms the last of a sub-group of metals whose melting-

and boiling-points fall with rising atomic weight. Cupric chloride and mercuric chloride, cupric sulphate and mercuric sulphate, resemble one another but slightly, as a consideration of their behaviour towards water will show. Even the resemblance between cuprous and mercurous chlorides is not so great as at first sight appears, and cuprous and mercurous oxides and sulphates differ very widely in stability. Similarly with lead and barium: PbO_2, the typical oxide of lead, is in no way analogous to BaO_2, and even PbO shows slightly acidic properties in utter contrast to BaO; also the metals themselves differ widely. With reference to silver and thallium, the oxide Tl_2O_3, although unstable, bears out the properties of the group type, and it is not surprising that the oxide and chloride Tl_2O and TlCl resemble other compounds of the same type. The chemical relationship of thallium to the alkali metals and to lead is, however, quite as great as to silver.

The placing of the elements of the rare earths in the existing periodic classification is also difficult. Scandium, yttrium, and lanthanum are properly placed in the third group; but the remaining elements, fourteen in number, are trivalent, though cerium, the first of their number, appears to be quadrivalent in its dioxide; they cannot, therefore, occupy positions in successive groups. Their atomic numbers (q.v.) place these elements in the following order: cerium (58), praseodymium (59), neodymium (60), illinium (61), samarium (62), europium (63), gadolinium (64), terbium (65), dysprosium (66), holmium (67), erbium (68), thulium (69), ytterbium (70), lutecium (71). These fourteen rare-earth elements intervene between lanthanum in the third group, and the newly discovered hafnium, which appears to be an analogue of zirconium, in the fourth group. Their existence involves a long period of thirty-two elements, and they are followed by elements beginning with tungsten, which complete this long period in the normal way.

POSITION OF THE INERT GASES OF THE HELIUM GROUP

The gases of the helium group, viz. helium, 4·00; neon, 20·18; argon, 39·94; krypton, 83·7; xenon, 131·3, are all monatomic, elementary substances, devoid of chemical activity. They therefore constitute the group of no-valency elements, and it is necessary to assign them a position in the periodic classification. At the time of their discovery it was thought by some that these gases could find no place in the periodic scheme, especially since argon could not be placed between potassium and calcium, as its atomic weight demanded.

On the other hand, even previous to the discovery of the new elements, it was suggested by Flawitsky and Thomsen that a group of elements probably exists whose electro-chemical characters are $\pm\infty$, and whose valency is 8 or 0. If the elements are arranged according to the periodic system, but on a cylindrical instead of on a plane surface, H and Li, F and Na, Cl and K, Br and Rb, I and Cs are respectively adjacent, the transition in each case being from an extremely electro-negative to an extremely electro-positive element. Now in the long periods the members of the eighth group serve as neutral transitional elements between Groups VII A and I B; and whilst they manifest a maximum valency of eight, their occurrence in the free state in nature, the resistance which they offer to combination, and the inertness of their compounds suggest at least some analogy to the properties of the no-valency elements of the helium group. It is not an unreasonable suggestion, therefore, that these latter elements should be interposed between the pairs of elements given above, to modify the extreme transition from non-metallic to metallic characteristics.

Thus the change from extremely electro-negative to extremely electro-positive properties will be made in each case through an element which is chemically indifferent, and has no valency. The existence of such an element is explained

on the electronic theory of valency by supposing that there are eight electrons in the outer shell or sheath of the atom, which form a stable system, so that the atom does not tend either to gain or lose electrons, and so to enter into chemical combination.

It is true that the law of octaves is destroyed by the interpolation of the elements of the helium group, but it will be seen from the following scheme that these five elements are thus suitably placed in the periodic table:

H 1·008	He 4·00	Li 6·94
F 19·0	Ne 20·18	Na 23·00
Cl 35·46	A 39·94	K 39·10
Br 79·92	Kr 82·9	Rb 85·4
I 126·93	Xe 130·2	Cs 132·8

Further support is given to this conclusion by data concerning the atomic volumes of argon, krypton, and xenon, which, in the liquid state, are approximately equal to 35. In accordance therewith, these elements find places on Lothar Meyer's curve of atomic volumes without changing the character of that curve; and thus they take a permanent place in the periodic system

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CHAPTER II

ATOMIC STRUCTURE AND VALENCY

The foundation of modern theories of atomic structure and valency was laid by Davy and Faraday when by their experiments on electrolysis they disclosed an intimate connection between electricity and matter. In 1834, thirty years after Dalton had formulated his theory, Faraday propounded his laws of electrolysis in which the " atomic " structure of elec-

tricity was implied, but not expressed, for he showed that in electrolysis his ions were always associated with a definite charge or multiple thereof.

Weber (1849) held remarkably modern views of electricity and its connection with atoms, and Johnstone Stoney (1874) associated each chemical bond during electrolysis with the passage of a fundamental and constant quantity of electricity. To this quantity, in 1891, he gave the name, " electron ".

The next important contribution was made by Crookes, just previous to 1880, when he commenced to study the phenomena of electric discharge through high vacua. The fluorescence of the glass of a " Crookes tube " containing a high vacuum, which is now recognized as the seat of origin of Röntgen rays, was explained by Crookes as due to the bombardment of the glass by particles of an attenuated form of matter, produced, as is now known, by the breaking down of the atoms of the gas originally contained in the tube into smaller constituent parts. Since they start from the cathode and travel in straight lines, these particles in motion are called **cathode rays.** Sir J. J. Thomson has shown that each of these particles is only about $\frac{1}{1800}$th of the mass of an atom of hydrogen, and that they move with a velocity approaching that of light. It is significant that the final effect in the exhausted tube is independent of the nature of the gas originally present.

The particles likewise possess electrical properties, for not only are they deflected from their course by a magnet, but a charge of electricity is found to accumulate on a receiver on which they impinge; further, they are able to pass through aluminium foil, and if the vacuum-tube is made of this metal, they will penetrate it and make their presence manifest in the external air, by exciting phosphorescence, by giving rise to certain electrical phenomena, and by acting on photographic plates.

The significance of these researches lies in the fact that these " corpuscles ", as Sir J. J. Thomson called them, were obtained free from encumbering atoms, and were recognized as units of negative electricity: they were, indeed, the elec-

trons of Stoney. Associated with atoms of matter they constitute Faraday's ions.

The electric discharge through a Crookes tube produces other phenomena of great importance. If the cathode be perforated, streams of particles appear travelling in the opposite direction to the cathode rays, i.e. from anode to cathode and through the perforations or " canals "; for this reason they were termed canal rays. They are positively charged atoms, whose study, in the hands of Sir J. J. Thomson, resulted in the method of positive ray analysis, and later in the mass spectrograph of Aston. The production of Röntgen or X-rays, and the resulting fluorescence has already been noted. The former were used by Moseley to lay bare the secret of atomic number, and later provided a method for elucidating the structure of solids. The fluorescence led Becquerel to study fluorescent uranium salts; this led directly to radioactivity. If we add to these Bohr's treatment of optical spectra, we have, in synopsis, the main lines of approach to the fundamental problem of atomic structure.

Radioactivity.—The subject of radioactivity is dealt with more fully later (Chap. XIV); only the main conclusions need be mentioned here.

The atoms of radioactive elements such as uranium, thorium, or radium, undergo spontaneous disintegration, emitting three types of radiation in the process. These are:

α-particles, shown by Rutherford to be identical with charged helium atoms, He^{++}, of mass 4,
β-particles, or free negative electrons,
γ-rays, which are X-rays of short wave-length.

The expulsion of α- or β-particles has a profound effect on the atom from which they came, for a new atom results which exists for a shorter or longer period before it itself undergoes transformation by similar changes to another atom, the process ending with atoms chemically identical with those of lead.

In all the changes examined, some 40 new atoms are pro-

duced, each having a definite mass value between the limits of the masses of uranium and lead atoms. In chemical properties, however, they correspond to ten elements only, five of these being already known, viz., thallium, lead, bismuth, thorium and uranium. Thus, by reason of their similar chemical properties, more elements than one are entitled to occupy one place in Mendeléeff's periodic classification, although the atomic mass differs from one element to the other. Such elements are *isotopes*.

The genetical relationships are given by the Law of Radioactive Displacement (Soddy); the new atom (or element) produced by expulsion of an α-particle is found in the periodic table two places to the left of the parent atom, i.e. in the direction of diminishing mass; expulsion of a β-particle produces a movement of one place to the right.

Isotopy of Non-radioactive Elements.—The fact that the possession of isotopes is not confined to radioactive elements is shown by the method of " positive-ray " analysis introduced by Sir J. J. Thomson, and elaborated by Aston.

This method depends upon the fact that when the molecules of a gas contained in a discharge tube in a rarefied condition are submitted to an induction-coil discharge they lose electrons or β-particles—the so-called cathode rays—and consequently become positively charged. These positively charged atomic residues, travelling in a direction opposite to that of the cathode rays, approach the cathode with great velocities, the magnitude of which will depend upon the distance from the cathode at which they started; and they are then made to pass onwards from the cathode through a copper tube of 0·1 mm. bore which pierces it. The pencil of rapidly moving positively charged particles thus produced is called a positive ray, and when this ray is submitted simultaneously to the action of magnetic and electric fields at right angles to each other, the particles are so deflected by the joint action of the two fields as to produce, on account of the differing velocities of the particles, a surface the projection of which

takes the form of a parabola. If the rays impinge upon a photographic plate they produce there a permanent record. Now all particles of equal mass, or, more strictly, for which the value $\frac{m}{e}$, where e is the electric charge, is the same, will form a single parabola; whilst the presence in the gas of particles of different masses will be shown by the formation of more than one parabola on the photographic plate. Thus the presence of different isotopes in an elementary gas is self-revealed photographically, when suitable arrangements are made for that purpose.

The first element made to exhibit isotopy in this manner was neon; for whilst elements previously examined gave single parabolas, neon gave a definitely double one. Now the positions of the parabolas is an indication of the relative masses of the particles producing them; and thus it was inferred that atmospheric neon, with atomic weight 20·2, is a mixture of an isotope of atomic weight 20 with a small proportion of a second isotope of atomic weight 22. So the isotope of neon, metaneon, was recognized.

This method has been brought to a greater state of refinement by Aston, in his mass-spectrograph, which sorts out a narrow beam of positive rays into a ribbon so that an effect like a spectrum is produced, the rays attributable to different isotopes appearing as successive lines upon the ribbon. Now since the positions of these lines depend partly upon the relative masses of the charged particles which cause them, this similitude of a spectrum, produced electrically, is called a *mass-spectrum*.

Comparison with the trace of a standard particle (e.g., the oxygen isotope of mass 16) enables the masses of the various particles to be found with an accuracy of 1 in 10,000.

Twelve elements still remain to be examined; of the remainder, twenty-two are simple, consisting of atoms of one mass, the others are isotopic. Some of the results are shown on the following page.

TABLE OF ELEMENTS AND ISOTOPES

Element.	Atomic Number.	Atomic Weight.	Mass numbers of Isotopes in order of intensity.
H ..	1	1·0078	1, 2, 3
He ..	2	4·002$_2$	4
Li ..	3	6·94	7, 6
Be ..	4	9·02	9
B ..	5	10·83	11, 10
C ..	6	12·003$_6$	12, 13
N ..	7	14·008	14, 15
O ..	8	16·0000	16, 18, 17
F ..	9	19·00	19
Ne ..	10	20·18	20, 22, 21
Na ..	11	23·000	23
Mg ..	12	24 30	24, 25, 26
Al ..	13	26·97$_0$	27
Si ..	14	28 0$_8$	28, 29, 30
P ..	15	30·98$_2$	31
S ..	16	32·06$_5$	32, 33, 34
Cl ..	17	35·457	35, 37, 39
A ..	18	39·94	40, 36
K ..	19	39·10$_5$	39, 41
Ca ..	20	40 09	40, 44
Sc ..	21	45 1$_5$	45
Ti ..	22	47·90	48, 50
V ..	23	50·95	51
Cr ..	24	52·04	52, 53, 50, 54
Mn ..	25	54·95	55
Fe ..	26	55·84	56, 54
Co ..	27	58·95	59
Ni ..	28	58·69	58, 60
Cu ..	29	63·55	63, 65
Zn ..	30	65·38	64, 66, 68, 67, 65, 70, 69
Ga ..	31	69·72	69, 71
Ge ..	32	72·60	74, 72, 70, 73, 75, 76, 71, 77
As ..	33	74 93$_4$	75
Se ..	34	79·2	80, 78, 76, 82, 77, 74
Br ..	35	79·91$_6$	79, 81
Kr ..	36	82·9	84, 86, 82, 83, 80, 78
Rb ..	37	85·4$_3$	85, 87
Sr ..	38	87·6$_3$	88, 86, 87
Y ..	39	88 9$_3$	89
Zr ..	40	91·2	90, 94, 92, (96)
Ag ..	47	107 880	107, 109
Cd ..	48	112·4$_0$	114, 112, 110, 113, 111, 116
In ..	49	114·8	115
Sn ..	50	118·70	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
Sb ..	51	121·76	121, 123
Te ..	52	127·5	128, 130, 126, 125, 124, 122, 123, 127
I ..	53	126·93$_2$	127
Xe ..	54	130·2	129, 132, 131, 134, 136, 128, 130, 126, 124
Cs ..	55	132·8$_1$	133
Ba ..	56	137·3$_6$	138, 137, 136, 135
La ..	57	138·9$_0$	139
Ce ..	58	140·2	140, 142
Pr ..	59	140·9	141
Nd ..	60	144·2$_5$	142, 144, 146, (145)
Hg ..	80	200·6$_0$	202, 200, 199, 198, 201, 204, 196
Pb ..	82	207·2$_2$	208, 206, 207
Bi ..	83	209·0$_0$	209

It will be observed that elements of odd atomic numbers rarely have more than two isotopes.

It is to be observed first of all that in a number of cases there are two or three isotopes, though often more, even eleven in one case.

The existence of isotopes of hydrogen and oxygen is noteworthy, for these elements are standards of mass. The accepted standard is now the oxygen isotope $O^{16} = 16$. (See also, deuterium.)

Further, it is observed that the mass-numbers of isotopes are given as whole numbers, and that the atomic weight of an element such as aluminium, which consists of a single isotope, is very nearly but not always quite a whole number. In the case of an element whose atomic weight is widely removed from a whole number it is clear that the fractional atomic weight is the average of the atomic weights of the constituent isotopes; e.g. Cl = 35·457 represents a mixture of Cl^{35}, Cl^{37}, and Cl^{39}.

It was at first supposed that the atomic weights of individual isotopes were exactly whole numbers referred to O = 16·0000; except, indeed, in the case of hydrogen, which, even when corrected for isotopy, is known to have the value H = 1·0081. (Aston, 1935.) That the atomic weight of helium was slightly less than four times that of hydrogen was attributed to " packing ", an actual loss of mass occurring, i.e. conversion of matter into radiation, when four hydrogen atoms condensed into one helium atom (see pages 58, 531).

It has now been shown, by greater refinement of measurement, that, due to the packing effect, single isotopic masses are not always exactly whole numbers; e.g. while $F^{19} = 19{\cdot}0000$, $Cl^{35} = 34{\cdot}98$, and $Cl^{37} = 36{\cdot}980$.

The widespread occurrence of isotopes raises doubts as to the accuracy of atomic weights determined by chemical methods. Aston's method is suitable for small amounts of an element, and extreme purity is not required, since purification on the basis of particle mass is accomplished automatically. The method does not supersede chemical methods, but rather supplements them, for, while Aston's method

separates isotopes and weighs individual atoms, chemical methods yield the average mass of the isotopes present, a value more useful in chemical analysis. Nevertheless, by photometric estimation of the intensity of isotope lines in the mass spectrum, the isotopic ratio may be determined and the average atomic weight calculated. The results are generally in good agreement with those from chemical methods.

Since accurately determined chemical atomic weights represent averages, the disturbing question arises whether such atomic weights may vary according to locality of material because of varying proportions between constituent isotopes.

In the case of radioactive elements and the end product, lead, this question is to be answered in the affirmative. For other elements, the answer depends on the extent to which the isotopic masses vary. Thus, the two isotopes of hydrogen, $H^1 = 1{\cdot}008$, and $H^2 = 2{\cdot}0136$, differ by nearly 100 per cent. Consequently, their chemical reactivities, so far as atomic mass is involved, will vary, and lead to variations depending on the source and also on the methods by which ordinary hydrogen is purified for chemical determinations. Some differences may therefore be expected for elements of low atomic weight, and it is not surprising that boron, whose isotopic mass numbers differ by 10 per cent, should give the chemical values, 10·847, 10·823 and 10·818 when obtained from three different sources.

For the remaining elements, so far as experience goes, the chemical atomic weight is " a true constant of nature ".

The bearing of the discovery of isotopy upon the periodic law must now be considered. The fundamental statement of the law of Mendeléeff was this. The physical and chemical properties of the elements are periodic functions of the atomic weights. Yet there are shown above numerous cases of chemical identity coinciding with considerable differences of atomic weight. Thus the original foundation of the periodic law is shaken by this new generalization. A difficulty had arisen previously, however, with regard to the qualification of

atomic weight to indicate properties. Thus chemists had consented to transpose the positions of argon and potassium, cobalt and nickel, and tellurium and iodine respectively, because properties forbade atomic weight sequence to be followed; the rather lame conclusion being reached that these pairs of elements furnished exceptions to the general rule.

Atomic Numbers.—Since atomic-weight values have been degraded from their pre-eminent position as criteria of chemical properties, and the periodic system appears thereby to have been thrown out of focus, the question arises as to whether there is any other property of an atom which is more truly fundamental than its atomic weight, and can therefore be utilized to restore that great generalization to the position it merits as the guiding principle of descriptive and systematic chemistry.

Already an answer to this question is in sight. The remarkable facts of isotopy, and the transitions through various periodic groups of an atom undergoing successive radioactive changes, are accounted for by the loss of electric charges. For Soddy's Law plainly shows that the change produced by loss of an α-particle of mass 4, and charge of 2 positive units, may be compensated by a further loss of two β-particles, or negative electrons of negligible mass. This suggests that content of electric charge rather than atomic mass is the fundamental criterion of an atom, and the suggestion is found by experimental research to be true.

The loss of an α-particle, according to Soddy's law, causes an atom to move two places backwards in the periodic table; so that if there are $2n$ places preceding a particular element in the table the loss of n α-particles by each atom of that element, if the same process could be continued successively, would bring the element to the beginning, that is to the place occupied by hydrogen. Further, since n α-particles correspond with $2n$ positive charges, it may be supposed that successive places in the periodic table correspond with successive increments of positive charge on the nuclei of the atoms concerned.

This assumption, based upon Rutherford's conception of the atom, was made by van den Broek; and the number of the element according to the numerical value of its atomic charge is called its *atomic number.*

The atomic numbers of the elements are thus shown:

H	He	Li	Be	B . . .	Ra	Act	Th	U-X_2	U
1	2	3	4	5 . . .	$(N - 4)$	$(N - 3)$	$(N - 2)$	$(N - 1)$	N

where N is the total number of elements.

The only evidence so far considered for these atomic numbers is Soddy's law; the numbers are developed by assuming that the law extends backwards out of the region of radioactivity into that of low atomic weights, a procedure which needs justification. Moreover, the magnitude of the terminal numbers is not furnished by Soddy's law. That depends on the precise number of elements intervening between the terminal and earlier elements in the periodic system. This most desirable information, which fixes the total number of elements existing between hydrogen and uranium, and so determines the magnitude of the terminal atomic numbers, has been furnished by a method of experimental research now to be described.

X-ray Spectra.—The emission spectra of the elements differ much in complexity. Whilst the flame spectra of the alkali-metals, for example, consist of few lines, the arc or spark spectra of the heavy metals, e.g. the spectrum of iron, are very complex, and contain many lines. The X-ray spectra of the elements are, however, much simpler, and provide very important evidence on the question of atomic numbers. These spectra are produced in the following way.

When a metallic target in an X-ray tube is bombarded by electrons, there is produced a general, continuous X-radiation containing all wave-lengths within certain limits. If, however, the bombarding electrons are of sufficiently high velocity, an emission radiation containing X-rays of a few wave-lengths only, and characteristic of the metal used as a

target, accompanies the general radiation. These characteristic X-rays may also be produced by irradiating an element in a beam of primary X-rays of suitable character. Such X-rays are therefore capable of yielding a simple and characteristic spectrum if they can be suitably dispersed.

Now all X-rays are of wave lengths some thousands of times shorter than the wave lengths of ordinary light rays, and special means have therefore to be found to separate such rays into a spectrum. A prism, or a diffraction grating ruled on glass, is useless for this purpose, but the cleavage face of a crystal of, say, potassium ferrocyanide, can be employed owing to the fact that the space-lattice of the crystal, that is the distance between similar parts in the crystal structure, is of the right order of length to diffract X-rays, just as a Rowland grating diffracts rays of ordinary light. This discovery, made by Laue, Friedrich, and Knipping in 1912, and elaborated by Professors Bragg, father and son, not only elucidates the atomic structure of crystals, but has furnished in the hands of Moseley (1913, 1914) the means of providing experimental evidence for atomic numbers by the study of the X-ray spectra of the elements.

In the case of elements not conveniently handled in the solid state their compounds may be employed. For example, a solid metallic chloride yields an X-ray spectrum containing lines characteristic not only of the metal, but also of chlorine.

The X-ray spectra of successive elements in the periodic system from sodium onwards have been found to consist each of a single strong line with one or more weaker lines; and the vibration frequencies (v) corresponding with these strong lines are connected together by the formula:

$$v = AQ^2,$$

where A is constant, and values of Q for successive elements are approximately successive whole numbers which are in each case a unit less than the number for the element, assuming that for aluminium is 13. An illustration will make this plain.

Element.	Atomic Weight.	Atomic Number.	Q
Titanium	48·1	22	20·99
Vanadium	51·06	23	21·96
Chromium ..	52·0	24	22·98
Manganese ..	54·93	25	24·99
Iron	55·84	26	24·99

Thus, in general, if N is the atomic number of an element, and v the vibration frequency of the principal line in its X-ray spectrum, whilst A is a constant, the following relationship holds:

$$v = A(N - 1)^2.$$

The simplicity of the X-ray spectra of successive elements, and the orderly movement of the principal line along the spectrum from the positions of lower to those of higher vibration frequency as the elements are traversed, are impressive facts, the explanation of which is to be sought in the constitution of the nuclei of their atoms. It will be remembered that van den Broek assumed that successive places in the periodic table corresponded with equal increments of positive charge on the nuclei of the atoms of the elements, N, the atomic number of an element being also the number of positive charges on the nucleus of its atom.

Moseley accepted this view, and summarized his work on the elements from aluminium to gold, thus:

1. Every element, from aluminium to gold, is characterized by an integer N which determines its X-ray spectrum.

2. This integer N, the atomic number of the element, is identified with the number of positive units of electricity contained in the atomic nucleus.

3. The atomic numbers for all the elements from aluminium to gold have been tabulated on the assumption that N for aluminium is 13.

4. The order of the atomic numbers is the same as that of the atomic weights, except where the latter disagrees with the order of the chemical properties.

5. Known elements correspond with all the numbers between 13 (Al) and 79 (Au), except 3. There are here three possible elements still undiscovered.

The last statement is now capable of extension. The atomic number of uranium, the last of the elements, is 92; therefore 92 and only 92 elements exist from hydrogen to uranium inclusive. It is well to consider more fully the significance of this fact.

In the periodic table of Mendeléeff vacant spaces were left for three missing elements, which were afterwards discovered; but it was impossible to know with certainty the total number of vacant spaces that should be left, because the rare-earth metals created a hiatus of unknown width. Indeed, in postulating twelve series of elements, Mendeléeff showed vacancies which should not be there.

Now by the work of Moseley the roll of the elements is at length prepared; and when recent discoveries are taken account of, it is seen to be incomplete for lack of only two elements: a halogen (85), and an alkali metal (87); though the latter, eka-caesium, has been reported.

Atomic number may be defined thus:

The atomic number of an element is the number of units of free positive electricity in the nuclei of its atoms.

This definition makes it clear that electric content and not atomic mass is the factor determining the properties of the elements; and so the conclusion of the whole matter as regards the evidence of atomic numbers is that the statement of the Periodic Law must be recast into the following form:

The physical and chemical properties of the elements and their compounds are periodic functions of the atomic numbers.

The statement that when the order of sequence of atomic weights does not follow that of chemical properties, the atomic numbers support the order according to chemical properties, affords welcome confirmation of what chemists have regarded as inevitable: that the pairs of elements, argon and potassium, cobalt and nickel, tellurium and iodine, must be placed in the

order here stated and not in atomic weight order, which is the reverse, since no redetermination of the atomic weights of these three pairs of elements as they occur in nature is likely ever to reverse the order of atomic weight sequence.

These discrepancies receive a satisfactory explanation in terms of isotopes. Argon is mainly A^{40} with only one per cent of A^{36}, hence its average atomic weight (39·94) exceeds that for potassium (39·1) in which the lower isotope, K^{39}, preponderates. It may be noted that the heavier isotope, K^{41}, is radioactive. In the case of nickel and cobalt, the former is complex, having a larger amount of the isotope, Ni^{58}; its chemical atomic weight (58·69) thus falls below that of cobalt (58·94). Iodine and tellurium are similar. The former is simple, the latter complex having isotopes which yield the average atomic weight, 127·58, whereas I = 126·93.

The Nuclear Atom.—Newton's idea of the atom, probably shared by Dalton, was that of a " massy, impenetrable particle ", incomparably hard. This cannon-ball theory could persist so long as the chemist knew the atom only as an undivided unit; for although there was reason to regard all kinds of atoms as manufactured articles, composed of hydrogen or " protyle ", there was no necessity to postulate any kind of structure for a body which manifested no internal properties, and which remained " unbroken and unworn ".

With the discovery of radiant matter by Crookes, however, and then of radioactivity itself, the case was altered. When it was really understood that a spectacle of atomic disintegration was being witnessed in the new phenomena, when α- and β-particles were known to be leaving the atoms of radium at unimaginable velocities, attempts were made to represent pictorially the structure of these atoms. The atom of hydrogen was represented as a hollow sphere, sparsely populated with electrons, which on account of their freedom of movement and the rarity of collisions between them, never left the sphere. The atom of radium, however, was a busy hive, swarming with electrons, rapidly moving and frequently col-

liding, some of which were consequently ejected from the body of the atom with such velocity as never to return.

That such was not a true picture was revealed by the experiments of Rutherford, Geiger, and their co-workers (1905-1911), when they bombarded the atoms of matter with α-particles. It has been shown by these workers that an α-particle ejected from a radioactive body at a velocity of 10,000 miles per second, travels in a straight line whether through a vacuum or a material medium such as a gas or aluminium foil. The atoms of the medium, therefore, offer no obstruction; the α-particle pursues its headlong way as if there were no material atoms in its path. It does not thread its way between the atoms; it pierces them, passing through them as a comet might pass through the solar system. Now this statement is not always true; there are rare exceptions to it, which have been brought to light in a remarkable manner.

The molecules of a gas which are encountered by a travelling α-particle become ionized, owing to the displacement of electrons; and it has been shown by C. T. R. Wilson that gaseous ions form centres of condensation of water from supersaturated aqueous vapour. In this way the path of an α-particle through a gas supersaturated with aqueous vapour actually becomes visible, when suitably illuminated, as a glistening track of mist. So it is discovered that whilst the large majority of the α-particles travel in straight lines, which could not be the case if they were deflected from their course by impact with every atom they encountered, a small proportion are sharply deflected or even turned back on their course. Any deflection is a sign that something has been hit, which is comparable in mass with an α-particle; and the only possible conclusion is that the α-particle has encountered the nucleus of an atom, since the planetary electrons are powerless to cause an α-particle to deviate from its rectilinear course. Further, since the deflections of the α-particle are so rare, occurring in the case of " two encounters out of many thousands " according to C. T. R. Wilson, it is concluded that the

nucleus of an atom is very small compared with the whole volume of the atom.

For these reasons, Rutherford (1911) described the atom as having a very small nucleus surrounded by revolving electrons, as the sun is surrounded by revolving planets. The planetary electrons thus occupy the space which constitutes the volume of the atom, whilst the mass of the latter is concentrated at the centre. As a whole the atom is neutral, the positive charge on the nucleus being equalized by the negative electrons which surround it. The radii of the nucleus and of the electron are now known to be of the order 10^{-13} cm., while the radius of the atom of which they are constituents is 10^{-8} cm.

Small though it be, the nucleus is composite; this inevitable conclusion results from the facts of radioactivity, and from Moseley's atomic numbers. In 1921, Aston stated that the primordial particles of which all neutral atoms are composed in equal numbers are: *electrons*, or atoms of negative electricity, and *protons*, or atoms of positive electricity, the proton being identical with the free hydrogen ion. Atom building became very simple. It is only necessary to incorporate in the nucleus sufficient protons to give the necessary atomic mass, at the same time adding the number of electrons required to diminish the total positive charge to that required by the atomic number. The nucleus thus contains both protons and electrons. To balance the net positive charge which results, electrons equal in number to the charge occupy orbits external to the nucleus. Thus the nucleus of the carbon atom will contain 12 protons and 6 electrons, possessing an atomic mass of 12, and a positive charge of 6 units. To balance this charge, 6 electrons are outside the nucleus.

Recently, however, two other important particles have been recognized, the *neutron*, a massive uncharged particle, and the *positron*, the positive counterpart of the electron. It is almost certain that views of nuclear structure will require modification, and, for that reason, further discussion is postponed to the section on nuclear transformations (Chap. XIV).

"The individuality of the atom resides in the nucleus", as manifested by mass and atomic number. As an entity, it is beyond the attack of our feeble chemical reactions, being protected therefrom by its planetary electrons, the sole exception being the hydrogen nucleus, H^+. The hardest X-rays may penetrate sufficiently close to glean some information, but, apart from spontaneous disintegration, the citadel itself only succumbs to the assault of massive particles. In this way arise the nuclear transformations referred to above.

The Bohr Theory.—One question remains to be considered: how are the electrons external to the nucleus arranged? To find an answer, the origin and relationships of the lines in emission spectra must be discussed.

The spectrum of glowing hydrogen was examined by Balmer (1885) who found that all the known lines of the spectrum were given by the formula:

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

where ν gives the frequency of the lines when $n = 3, 4, 5 \ldots$, R being a constant.

Now, in accordance with Maxwell's electromagnetic theory, light was produced by vibrating electric charges. If then a hydrogen atom consisted of a massive positive nucleus with an electron circling round it, the spectrum of hydrogen should be due to the rotating electron. Such an electron would continuously lose energy due to the radiation it was emitting, and so would spiral towards the nucleus with increasing angular velocity. A continuous, not a line spectrum should be emitted, and the hydrogen atom would not be a permanent structure.

In 1913, Bohr advanced two postulates which at once gave some reason for atomic stability, correlated known facts of spectroscopy, and led to great advances bearing on atomic structure and chemical properties.

Firstly, he assumed that in certain selected orbits the electron could rotate round the nucleus without emitting energy.

These are *stationary orbits* or *states*, or *energy levels*; not that the electron is stationary, but no radiation occurs. Only such orbits were selected as had an angular momentum equal to $nh/2\pi$, where h is Planck's constant, and $n = 1, 2, 3 \ldots.$ The number n thus defines the orbit, and is known as the *principal quantum number*.

Secondly, he affirmed that monochromatic radiation of frequency ν was emitted only when an electron jumped from one stationary orbit to another nearer the nucleus. The energy radiated is the difference between the energies E_1 and E_2 of the two orbits, and is defined in the quantized relationship

$$E_1 - E_2 = h\nu.$$

Bohr's theory led to the expression:

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

for the frequencies of the spectral lines of hydrogen, where m and e are, respectively, the mass and charge of an electron, and h is Planck's constant. This is Balmer's formula in a generalized form, and by substituting the known values of m, e, and h, Balmer's empirical constant was got with great exactness.

Bohr's formula indicates that various series of lines should be emitted by hydrogen, and some lines in each of the following series have been observed, the calculated frequencies got by putting whole number values for n_1 and n_2 agreeing with those experimentally determined.

	Series.	n_1.	n_2.
(1885)	Balmer	2	3, 4, 5, etc.
(1909)	Paschen	3	4, 5, 6, etc.
(1914)	Lyman	1	2, 3, 4, etc.
(1922)	Brackett	4	5, 6.

On Bohr's mechanism these series arise thus. The electron in the normal hydrogen atom occupies the orbit of lowest energy where $n = 1$. When these atoms absorb energy, e.g.

in a Geissler tube, their electrons move to orbits of greater energy where n may be 2, 3, 4, etc. On their return in jumps to lower orbits they emit the energy which gives rise to the spectrum. Those returning to the first orbit ($n = 1$) give rise to the Lyman lines in the far ultra-violet, to the second ($n = 2$), the Balmer series, to the third ($n = 3$), the Paschen series, and to the fourth ($n = 4$), the Brackett series deep in the infra-red. The intensity of a given line will depend on the number of electrons per unit time interval which perform the jump causing the line, and on the value of the energy quantum emitted.

The orbits may be circular or elliptical.

Circular orbits.—The permissible orbits are defined by the integer n, and Bohr showed that their radii were in the ratios, $1 : 4 : 9 \ldots n^2$.

Elliptical orbits.—It was pointed out by Sommerfeld that the fine structures of hydrogen spectral lines could be explained if some of the orbits were elliptical. A circular orbit defined by n may be replaced by an infinite number of elliptical orbits having the same energy. These would have the same major axis, but differing eccentricities. Only certain ellipses are permissible, their eccentricities being defined by an integer k, the *subsidiary* or *second quantum number*, such that

$$\frac{n}{k} = \frac{\text{major axis}}{\text{minor axis}}.$$

For $n = 4$, k may be 4, 3, 2, 1. The values of k are in order of increasing ellipticity, for when $k = n$ the orbit is circular.

Magnetic Quantum Number.—The magnetic perturbation of spectral lines introduces still another quantum number. When a source of light yielding a spectrum is subjected to a powerful magnetic field the lines of the spectrum undergo a change. If the light is viewed in the direction of the field, each line is doubled; if viewed at right angles to the field, each line appears tripled, i.e. the original line is seen with a line on either side of it. This effect, discovered by Zeeman

(1896), may be explained on Bohr's model thus. The electron orbits are no longer confined to one plane, but under the influence of the magnetic field may be found in various planes. The number of possible planes is limited by quantum conditions, and they are defined by a third number, the *magnetic quantum number*, m.

Spin Quantum Number.—For satisfactory explanation of the facts of spectroscopy and of the periodic classification of the elements, there is introduced a fourth number, the *spin quantum number* s, which may be either $+\frac{1}{2}$ or $-\frac{1}{2}$. This number may be interpreted as being due to the spin of the electron about its own axis. According to Heitler and London, the sharing of two electrons in a covalent bond is a neutralization or coupling of opposite spins.

On this model of the hydrogen atom the electrons rotate round the nucleus in orbits selected by the quantum numbers, n, k, and m, the number s being due to the electron spin. Only one electron may occupy one orbit at a time. A more satisfactory development of energy levels, and of the four quantum numbers, is achieved by the newer theories of quantum mechanics, and in a more usual notation Bohr's subsidiary quantum number k is replaced by the integer l, such that $l = (k - 1)$.

Thus, for the principal quantum number n, l may be $0, 1, 2, 3, \ldots (n - 1)$. The magnetic quantum number m may have the values $-l$ to $+l$. Thus when $l = 2$, m may be $2, 1, 0, -1$, or -2. The spin quantum number may be $\pm\frac{1}{2}$.

Electronic Configuration.—The assignation of correct electronic quantum numbers for atomic systems more complex than hydrogen may be made on the basis of Pauli's Exclusion Principle, according to which no two electrons in one atom may have the same four quantum numbers. On the chemical side, the atom structures must conform to their properties as exhibited in the periodic classification. As early as 1924, Main Smith was able, largely from chemical

evidence, to assign electronic structures to each atom, and to propound a Law of Uniform Atomic Plan. According to this law, the atomic structures of all elements follow the same constitutional plan as their predecessors in order of atomic numbers.

In any atom, electrons having the same principal quantum number, n, form quantum groups distinguished as the first, second, etc., quantum group according to the value of n, or as the K, L, M, etc., shell or energy level. The maximum numbers found in the first five groups or shells are exhibited in the inert gas radon, or radium emanation.

Quantum group	1	2	3	4	5	6
Shell or level	K	L	M	N	O	P
Radon At. No. 86	2	8	18	32	18	8

The subsidiary number, l, affords a basis for subdivision, the maximum number of electrons in each sub-group depending on its value, $l = 0, 1, \ldots (n - 1)$. In spectroscopy, these sub-groups are sometimes referred to as the s, p, d, f sub-groups. Thus in the fourth quantum group, or N shell, of radon, there are four sub-groups containing the maximum number of electrons for $l = 0, 1, 2$, or 3, thus:

Sub-groups (nl)	4, 0	4, 1	4, 2	4, 3
	$4s$	$4p$	$4d$	$4f$
No. of electrons	2	6	10	14

The sub-groups may be further divided, but for most purposes the scheme shown is ample, and is that used in the table on p. 66. It applies, of course, only to normal, uncombined and unexcited atoms.

For an atom whose electrons are in the first quantum state, $n = 1$, $l = 0$, $m = 0$, $s = \pm\frac{1}{2}$. The hydrogen electron appears therefore in the first quantum group (K shell). So also do the two helium electrons, because their spins are $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively.

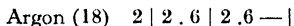
The K level is filled since all the possible quantum numbers for $n = 1$ are utilized. It is present in all succeeding atoms,

as is shown by Moseley's work on X-ray spectra. Lithium, with three electrons, may have 2 in the first quantum group, but must place the third in the second quantum group, where $n = 2$ and $l = 0$ or 1. Passing along the short period

Li Be B C N O F Ne,

successive additions bring the electron content of the second group or L shell up to 8 in neon.

Chemical properties and quantum theory alike indicate that the L shell is now complete for all possible quantum numbers have been utilized, hence the additional sodium electron goes to the third quantum group. Passing along the next short period, the inert gas argon marks a stage in the filling of the M shell, thus:

Argon (18) 2 | 2 . 6 | 2 .6 — |

In the extended form of the periodic classification at the end of this book, it will be observed that the following series of elements are marked off from the others.

1st long period	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
2nd long period	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag
3rd long period	La(R.E.)	Hf	Ta	W	Re	Os	Ir	Pt	Au

Rare earth elements (R.E.):

Ce	Pr	Nd	Il	Sm	Eu	Gd
Tb	Dy	Ho	Er	Tm	Yb	Lu

These are *transitional* series of elements in which the simple method of building electronic structures is interrupted.

The electronic structures of calcium, scandium, and copper are:

	K	L	M	N
Ca(20)	2	2 . 6	2 . 6 —	2
Sc(21)	2	2 . 6	2 . 6 . 1	2
Cu(29)	2	2 . 6	2 . 6 . 10	1

Although the N shell exists in calcium, its expansion is prohibited until copper is reached, the additional electrons going into the M shell and increasing its content from 8 to 18 electrons.

A similar change in the mode of development occurs in the two series headed by yttrium and lanthanum (excluding the rare earth elements). Again the second last group expands at the expense of the outer group.

The lanthanum series is complicated by the rare earth elements which follow La in order of atomic number.

Consider the structures:

	K, L, M	N	O	P
Ba(56)	28 electrons	18	8	2
La(57)	,, ,,	18	9	2
Ce(58)	,, ,,	19	9	2
Lu(71)	,, ,,	32	9	2
Hf(72)	,, ,,	32	10	2

No sooner has the expansion of the O shell commenced in lanthanum, than the expansion of the N shell commences in cerium. This continues through the rare earth elements until lutecium is reached, thereafter the expansion of the O shell continues until in gold it contains 18 electrons.

There are thus definite points when the development of outer shells, or quantum groups ceases, while the atoms acquire stability by buttressing their inner groups.

The division of all atoms by Bohr into four types is amply confirmed by chemical character.

1. Atoms having all electronic groups completed (i.e. with closed shells). These are the inert gases which never gain electrons but may lose them, e.g. in a Geissler tube.

2. Atoms where every group save the highest is complete. These are found in the elements of the first two short periods, excluding the inert gases, and in elements such as those of Groups I A, II A and B sub-groups.

3. Atoms whose two outer shells are incomplete. These are the elements considered above; the transitional elements in the wider sense. They are catalysts, they display polyvalency, and occupy the hollows in Lothar Meyer's atomic volume curve. Their ions are coloured and paramagnetic.

4. Atoms in which the three last shells are incomplete.

DISTRIBUTION OF ELECTRONS IN THE ATOMS

Element		K	L		M			N	
		1, 0 1*s*	2, 0 2*s*	2, 1 2*p*	3, 0 3*s*	3, 1 3*p*	3, 2 3*d*	4, 0 4*s*	4, 1 4*p*
H	1	1	—	—	—	—	—	—	—
He	2	2	—	—	—	—	—	—	—
Li	3	2	1	—	—	—	—	—	—
Be	4	2	2	—	—	—	—	—	—
B	5	2	2	1	—	—	—	—	—
C	6	2	2	2	—	—	—	—	—
N	7	2	2	3	—	—	—	—	—
O	8	2	2	4	—	—	—	—	—
F	9	2	2	5	—	—	—	—	—
Ne	10	2	2	6	—	—	—	—	—
Na	11	Neon Configuration			1	—	—	—	—
Mg	12				2	—	—	—	—
Al	13				2	1	—	—	—
Si	14				2	2	—	—	—
P	15				2	3	—	—	—
S	16				2	4	—	—	—
Cl	17				2	5	—	—	—
A	18				2	6	—	—	—
K	19	Argon Configuration					—	1	—
Ca	20						—	2	—
Sc	21						1	2	—
Ti	22						2	2	—
V	23						3	2	—
Cr	24						5	1	—
Mn	25						5	2	—
Fe	26						6	2	—
Co	27						7	2	—
Ni	28						8	2	—
Cu	29						10	1	—
Zn	30						10	2	—
Ga	31						10	2	1
Ge	32						10	2	2
As	33						10	2	3
Se	34						10	2	4
Br	35						10	2	5
Kr	36						10	2	6

Element	Configuration of Inner Shells	N		O			
		4, 2 $4d$	4, 3 $4f$	5, 0 $5s$	5, 1 $5p$	5, 2 $5d$	6
Rb 37	Krypton Configuration	—	—	1	—	—	–
Sr 38		—	—	2	—	—	–
Y 39		1	—	2	—	—	–
Zr 40		2	—	2	—	—	–
Cb 41		4	—	1	—	—	–
Mo 42		5	—	1	—	—	–
Ma* 43		6	—	1	—	—	–
Ru 44		7	—	1	—	—	–
Rh 45		8	—	1	—	—	–
Pd 46		10	—	—	—	—	–
Ag 47	Palladium Configuration		—	1	—	—	–
Cd 48			—	2	—	—	–
In 49			—	2	1	—	–
Sn 50			—	2	2	—	–
Sb 51			—	2	3	—	–
Te 52			—	2	4	—	–
I 53			—	2	5	—	–
Xe 54			—	2	6	—	–
Cs 55	The shells $1s$ to $4d$ contain 46 electrons		—	The shells $5s$ to $5p$ contain 8 electrons		—	1
Ba 56			—			—	2
La* 57			—			1	2
Ce* 58			1			1	2
Pr* 59			2			1	2
Nd* 60			3			1	2
Il* 61			4			1	2
Sm* 62			5			1	2
Eu* 63			6			1	2
Gd* 64			7			1	2
Tb* 65			8			1	2
Dy* 66			9			1	2
Ho* 67			10			1	2
Er* 68			11			1	2
Tm* 69			12			1	2
Yb* 70			13			1	2
Lu* 71			14			1	2

Element	Configuration of Inner Shells	O		P			Q
		5, 2 5*d*	5, 3 5*f*	6, 0 6*s*	6, 1 6*p*	6, 2 6*d*	7, 0 7*s*
Hf* 72	The shells 1*s* to 5*p* contain 68 electrons	2	—	2	—	—	—
Ta* 73		3	—	2	—	—	—
W 74		4	—	2	—	—	—
Re* 75		5	—	2	—	—	—
Os* 76		6	—	2	—	—	—
Ir* 77		7	—	2	—	—	—
Pt 78		8	—	2	—	—	—
Au 79	The shells 1*s* to 5*d* contain 78 electrons		—	1	—	—	—
Hg 80			—	2	—	—	—
Tl 81			—	2	1	—	—
Pb 82			—	2	2	—	—
Bi 83			—	2	3	—	—
Po 84			—	2	4	—	—
( )* 85			—	2	5	—	—
Rn 86			—	2	6	—	—
( )* 87	Radon Configuration					—	1
Ra* 88						—	2
Ac* 89						1	2
Th* 90						2	2
Pa* 91						3	2
U* 92						4	2

The table shows not only those distributions of electrons which have actually been ascertained from the spectra, but also those which have been determined by considerations of analogy; the latter are indicated by an asterisk attached to the symbol of the element. The probability of correctness of the inferences from analogy is, however, very high.

Table copied, by permission, from *Atomic Physics*, by Max Born.

These are the rare earth elements which form an inner transitional series. They are remarkable for their characteristic tervalency, are catalysts, and may yield coloured and paramagnetic ions.

Chemical properties therefore depend on the electrons in the outermost shells, from which valency electrons are drawn; the inner shells remain inviolate.

ELECTRONIC THEORY OF VALENCY

It will be recalled that in Faraday's Laws of Electrolysis, which plainly showed the connection between the charge and the valency of the ions transporting the current, there lay buried the germ of the electronic theory of valency. Then Arrhenius carried the idea a stage further by supposing that electric charge did not depend on the advent of the electric current, but rather that the passage of the current in electrolysis depended on the previous existence of charged ions in the solution. Electricity was so near the surface, so to speak, in a solid electrolyte, that it broke through and manifested itself directly the electrolyte was dissolved in water.

The work of Crookes confronted the chemist with the fact that on the surface of atoms there are electrons which are removable, and that this constitutes the secret of all electrochemical theories from the days of Davy. These transferable electrons are the active agents in chemical change, they are the stuff of which valency is made; they are valency electrons. This idea was first realized by Ramsay who may thus be said to have originated the electronic theory of valency.

According to Ramsay, the atoms of sodium and chlorine are held together by means of an electron E, so that the formula for sodium chloride may be written, NaECl. On solution in water a separation takes place, the sodium atom loses its share of E which goes over completely to the chlorine atom. There results a positively charged sodium ion Na^+ because of deficiency of E, the unit negative charge, and a negatively charged chloride ion Cl^- which owes its charge to excess of E, thus:

$$NaECl \rightleftharpoons Na^+ + ECl^-.$$

Thus far, however, it is not apparent why the sodium atom, rather than the chlorine atom, should yield its share of the electron, or indeed, why anything should happen at all. It has already been suggested that the periodic classification

furnishes the criterion of valency, therefore the distribution of valency electrons in the successive elements of a period must be connected with the transition of chemical properties along that period. Consider the period sodium to argon.

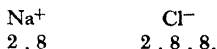
I	II	III	IV	V	VI	VII	O
Na	Mg	Al	Si	P	S	Cl	A

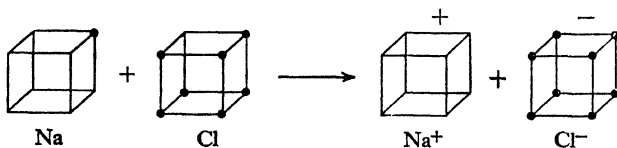
The number of electrons in the outer shell of a neutral atom in this period corresponds with the group in which the element occurs. Thus, sodium has one electron in its outer group, magnesium two, and so on, up to the argon atom which has eight. Now, the possession of eight electrons in the outer shell corresponds with chemical inertness and null-valency, such as characterizes argon and other members of the same family. It is thus a condition of stability which, it is believed, the atoms of elements tend to attain by loss or gain of electrons. Atoms possessing up to three electrons in the outer shell generally prefer to lose them rather than to gain a larger number so as to make up the full complement of eight; by losing their outer electrons they sometimes unmask a group of 8 (or 18) contained in the second outermost shell. An atom with four outer electrons may lose these, or gain other four, though, as will be seen later, the tendency is rather to acquire four; if it has more than four, then it is easier to gain the smaller than to lose the larger number. Elements whose atoms lose electrons are electropositive and are metals, the atoms becoming positive ions. In like manner an atom which gains electrons becomes a negative ion, and the element concerned is electronegative and a non-metal. Eight electrons constitute an octet, and the theory above expounded is the *octet theory* advanced independently by Kossel and Lewis in 1916.

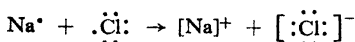
The number 8 recalls the normal and contravalency of Abegg (1904), who indicated that it was significant for all atoms as the number "representing the points of attack of electrons". In the same year, Sir J. J. Thomson, from his model of the atom, deduced mathematically that eight elec-

trons should form a stable grouping. It is interesting to note that the cubic formulæ given below were used by Lewis as early as 1902.

The interaction of sodium and chlorine may now be considered, and it will be seen what advance has been made on Ramsay's theory. The activity of metallic sodium depends on the ease with which it gets rid of its solitary valency electron so that the shell of eight electrons below may now become the outer shell; whilst the activity of the chlorine atom is due to the tendency to acquire one electron which, together with the seven outer electrons it already possesses, will form a completed octet. Thus, the vigorous reaction between sodium and chlorine is due to the transfer of one electron from the sodium to the chlorine atom, whereby sodium and chloride ions are formed. The electron arrangement in each ion will thus be:

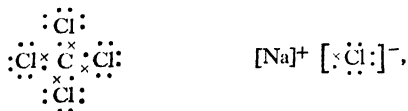
Na^+	Cl^-
2 . 8	2 . 8 . 8.

These are the configurations of the neutral atoms of neon and argon, respectively.

It is generally sufficient to represent only the changes in the outer electrons, the valency electrons. Thus the octet was formerly represented spatially by the corners of a cube (Lewis).

A simpler plan is to affix dots to the symbols or formulæ to represent electrons, thus:

$$\mathrm{Na}^{\bullet} + .\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \rightarrow [\mathrm{Na}]^+ + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^-$$

This idea represents a fundamental change in our con-

ceptions of electrolytes. Whereas Arrhenius supposed that salts like sodium chloride must dissolve in an ionizing solvent such as water before they formed ions, the truth is that ions are formed by the very process of chemical reaction. Consequently sodium chloride consists of ions, and in the solid state these are held together by electrostatic attraction. Solution in water merely causes a separation of these ions, and the crystalline structure disappears. The electrolyte need not be soluble in water, for X-ray analysis of crystal structure reveals, for example, that many oxides are ionic in character. Thus magnesium oxide contains magnesium and oxide ions, $[\text{Mg}]^{++}$ and $[{}^{\times}_{\times}\ddot{\underset{\cdot\cdot}{\text{O}}}:]^{=}$, packed in characteristic manner in the solid. The electrons marked x are those acquired by oxygen from magnesium in the process of reaction.

There are, however, other compounds which are not electrolytes, e.g. CH_4 and CO_2, and the theory advanced by Lewis is sufficiently wide to include these. If the formation of a compound is contingent on the acquirement of an octet of electrons, then completed octets may arise by mutual sharing of electrons between the atoms, without any transference, and without the development of electro-polarity of the type just considered. According to this view the difference between CH_4, or better, CCl_4, and NaCl will be represented thus:

```
         ..
        :Cl:
     ..  .x  ..
    :Cl:x C x:Cl:            [Na]+ [x.Cl:]-,
     ..  x.  ..                     ..
        :Cl:
         ..
```

where (x) marks electrons contributed by carbon and sodium, respectively.

The kind of valency in which a pair of electrons, called a *duplet*, is shared equally between two atoms, each of which has provided one electron, is called *co-valency*: whilst that kind in which complete transference of an electron has occurred, producing ionization, is called *electrovalency*. It thus

appears that these two types of valency satisfy respectively the unitary doctrine of Dumas, and the dualism of Berzelius and Arrhenius. The controversy between Dumas and Berzelius which ended in the discomfiture of the latter, is now resolved, and it is recognized that both were correct in their own sphere. The characteristic valency shown by organic compounds is covalency, and therefore, in the language of Dumas, these compounds form a complete whole and cannot be said to consist of two parts. On the other hand, inorganic compounds generally display electrovalency and ionic reactions.

There is yet, however, another method of union which must be considered. It should be remembered that the formulæ given above represent an enormous simplification of the properties of the electron; it is neither stationary nor is it a minute point of electricity, for it is now considered to be associated with a wave motion. In addition, the duplet link may not be symmetrically disposed towards the two atoms which it links together, the part towards which it has moved being negatively charged, and the other part positively charged, with development of incipient polarity. Such molecules or links are termed *polar*, and the segregation of electrical charges will produce a dipole moment in the molecule. For clarity, the term polar should not be regarded as synonymous with electrovalent, although electrovalency is extreme polarity. In addition, an unsymmetrical arrangement of atoms round a central atom may endow the molecule with a considerable dipole moment. It is possible, therefore, for a molecule whose primary valencies are satisfied by the methods described above to possess secondary, residual, or field valency, in virtue of which it may attract other similar molecules and form complexes which are held together by the electrostatic attraction of oppositely charged centres.

Nevertheless, there are a large number of compounds in which this " secondary " valency may be precisely expressed in terms of electrons.

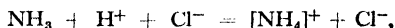
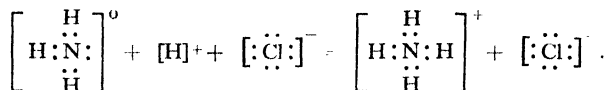
The electrically neutral molecule of ammonia may be represented thus:

$$\begin{array}{c} \text{H} \\ \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}: \\ \text{H} \end{array}$$

the nitrogen octet containing five of its own electrons, and, in addition, three derived from the hydrogen atoms. Two of these electrons are disengaged and form a " lone pair ", as they are called. The suggestion was made by Huggins (1922), and later developed extensively by Sidgwick, that these two electrons might be donated to another atom so that it might acquire an inert gas configuration. Now ammonium chloride is formed thus:

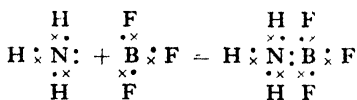
$$NH_3 + H^+ + Cl^- = [NH_4]^+ + Cl^-,$$

or electronically,

$$\left[\begin{array}{c} \text{H} \\ \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}: \\ \text{H} \end{array}\right]^0 + [\text{H}]^+ + [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:]^- = \left[\begin{array}{c} \text{H} \\ \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:\text{H} \\ \text{H} \end{array}\right]^+ + [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:]^- .$$

It will be observed therefore that the hydrion H^+, now has a share of two electrons, and in electronic structure compares with the inert gas helium, which also has two electrons. For the first few electropositive elements therefore, the helium pair confers the same stability as does the octet in later elements. At the same time the positive charge of the hydrion is now transferred to the ammonium ion.

Whether a lone electron pair will be reactive or not depends on the character of the central atom, for PH_3 has little attraction for H^+, and with AsH_3 and SbH_3 the attraction does not exist.

Ammonia may also combine with complete molecules, e.g. BF_3, forming molecular compounds. In BF_3 boron has not a completed octet, and so may accept the two electrons provided by the nitrogen atom in NH_3, thus:

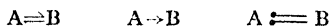
$$\begin{array}{c} \mathrm{H} \\ \times\bullet \\ \mathrm{H} \,\dot{\times}\, \mathrm{N}: \\ \bullet\times \\ \mathrm{H} \end{array} + \begin{array}{c} \mathrm{F} \\ \bullet\times \\ \mathrm{B} \,\dot{\times}\, \mathrm{F} \\ \times\bullet \\ \mathrm{F} \end{array} \rightleftharpoons \begin{array}{c} \mathrm{H}\ \ \mathrm{F} \\ \times\bullet\ \bullet\times \\ \mathrm{H} \,\dot{\times}\, \mathrm{N} : \mathrm{B} \,\dot{\times}\, \mathrm{F} \\ \bullet\times\ \times\bullet \\ \mathrm{H}\ \ \mathrm{F} \end{array}$$

According to Lowry, one of the electrons of the lone pair is transferred to the other molecule concerned so that polarity results, the donor molecule becoming positive, and the acceptor molecule becoming negative. The other electron is shared equally by both. Thus the bond is half polar and half non-polar. Lowry therefore calls the bond so formed a *semipolar double bond.*

Whatever the mechanism of its formation, this bond is that by which molecular compounds are formed, including many ammines and hydrates. It is Werner's auxiliary valency and may be known as *co-ordinate covalency* (Sidgwick).

It is believed that a fourth type of link exists, the monoelectronic link. This will be considered in certain specific examples, e.g. the boron hydrides.

Some remarks may now be made on the use of " bonds ". In organic chemistry the use of bonds to represent the known molecular constitution of organic compounds has been of great value; in the case of inorganic compounds their use has been less satisfactory, and even misleading. It will be apparent that compounds whose parts are held together by electrovalency, i.e. electrolytes, should not be represented as having bonds, since union is by a diffused electrostatic attraction and not by a localized force transmitted through an electron pair. A bond (—) therefore, should only be employed to represent reciprocal covalent union, such as is common in organic compounds, and which also occurs in a number of inorganic compounds and radicles. This bond is sometimes replaced by a dot (·) when no confusion with electronic formulæ may arise. The "semipolar double bond " is of the covalent type, although both electrons originate from the same atom, and for it Lowry employs the sign ($\rightleftharpoons$), the half-arrow representing the direction of transfer of the one electron, and the plain

bond the mutual sharing of the other electron. Sidgwick* uses the sign (→), the arrow pointing away from the atom which provides the electrons. Another scheme suggested by Main Smith, represents each electron in the link, thus, $\stackrel{\bullet}{=}$, the dot being near the atom which provided the electron. A co-ordinate covalency may therefore be represented in three ways.

$$A \rightleftharpoons B \qquad A \rightarrow B \qquad A \stackrel{\bullet}{=} B$$

On Main Smith's formulation a single covalent bond would be represented thus:

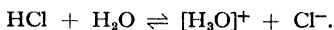
$$A \leftrightharpoons B$$

The connection between the new theory and Abegg's doctrine of valency becomes apparent. Consider the two compounds of phosphorus, PH_3 and P_2O_5. Abegg would say that the normal valency of P is -3 and its contravalency $+5$, with an arithmetic sum of 8. Which valency is to be considered normal and which contra- is of minor importance. What is important is that the phosphorus atom is electronegative towards hydrogen, receiving from three atoms of this element the three electrons necessary to complete its octet; and electropositive towards oxygen, so that two phosphorus atoms each contribute five electrons to complete the octets of five oxygen atoms, each of which possesses six electrons.

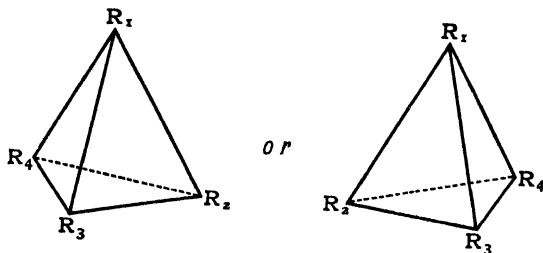
Properties Associated with Links.—Molecules whose atoms are linked covalently will have but a small external field of force, hence the work necessary to separate them in volatilization will be small: such compounds therefore have low boiling-points. It will be otherwise with electrovalent compounds whose full ionic charges are utilized in binding the ions. Thus $SiCl_4$ boils at 57° and NaCl at 1440°. The increase of boiling-point consequent on polymerization should be distinguished from that due to electrovalency. Moreover, covalent compounds are soluble in organic solvents, and are poor conductors of electricity in solution and in the fused state, whereas good conductivity is an ionic characteristic. Some

* *The Electronic Theory of Valency.*

compounds show a dual character. Anhydrous liquid hydrogen chloride is not a conductor, whereas in aqueous solution it is a good conductor. Presumably electrovalent conditions arise in water due to the formation of oxonium ions thus:

$$HCl + H_2O \rightleftharpoons [H_3O]^+ + Cl^-.$$

Similarly, $AlCl_3$ is low melting and a poor conductor, nevertheless it forms conducting aqueous solutions. Most likely hydration occurs with the formation of the ions $[Al(H_2O)_6]^{+++}$ and $3Cl^-$.

On occasion, therefore, one form may change abruptly to the other. Chemical theory accepts the view that covalency and electrovalency are the limiting conditions of various intermediate gradations. The present theories of crystal and molecular structure recognize the two types, and clearly indicate that gradations are possible.

The covalent bond possesses direction in space and for this reason isomeric molecules exist having the same empirical composition but having differing properties explicable only in terms of the different space distribution of constituent atoms and groups. This is familiar in the stereo-isomerism and in the optical activity of organic compounds. Taking a compound of the type $CR_1R_2R_3R_4$, the four univalent radicles may be regarded as grouped about the carbon atom, occupying mean positions. Unless all the groups lie in one plane with the carbon atom a tetrahedral arrangement results, the groups R_1, R_2, R_3, and R_4 forming the apices of a tetrahedron. The spatial configuration becomes:

The molecules thus indicated are " asymmetric ", possessing no plane of symmetry, and though the compounds are of the same composition, they are not identical, the structures being related to one another as object and image, or as a right-handed and a left-handed screw. This difference is expressed in their effect on polarized light, and when transparent, such substances, whether in solution or not, rotate the plane of polarized light, the one compound to the left, the other an equal amount to the right. They are said to be *enantiomorphous.*

Similar space relationships are to be found in inorganic compounds, which are in no way inferior to carbon compounds in the symmetry of their varied architecture. This will be dealt with in connection with Werner's complex salts (Chap. XII).

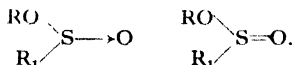
It may be noted that asymmetric, and therefore optically active compounds analogous to the carbon type above are known, when the central atom is nitrogen, silicon, phosphorus, sulphur, selenium, arsenic, copper or zinc. In addition, though not with carbon, optical activity may arise when the central atom is associated with groups having an octahedral space disposition.

The semi-polar bond (co-ordinate covalency) induces properties resembling, though to a lesser degree, those associated with an electrovalent bond. The main evidence for its existence may be briefly mentioned. It has already been noted that Sugden's parachor is additive, and may even distinguish the increment due to the type of bond present. For the covalent double bond (4 electrons), and for the semi-polar bond (2 electrons), in

$$\begin{array}{ccc} \mathrm{A} \quad \mathrm{B} & \text{and} & \mathrm{A} \rightleftharpoons \mathrm{B} \\ +\,23{\cdot}2 & & -\,1{\cdot}6 \end{array}$$

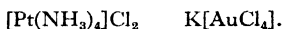
the differences between the observed and calculated molecular parachors give distinct values for each type, as shown above.

On parachor evidence the sulphinic esters are represented by the first formula:

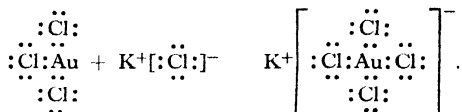
$$\begin{array}{l} RO \\ \quad \rangle S \rightarrow O \\ R_1 \end{array} \qquad \begin{array}{l} RO \\ \quad \rangle S = O. \\ R_1 \end{array}$$

This conclusion is confirmed by the discovery that these molecules are asymmetric and show optical activity, hence the arrangement must be tetrahedral, even although only three groups are present. This result is not possible if a double bond be present, for all the atoms would be in one plane.

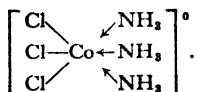
The term " co-ordination " was used by Werner in his theories of the structure of molecular compounds such as the ammines and related complex salts.

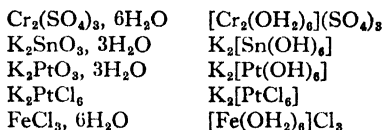
The compounds, $PtCl_2,4NH_3$ and $AuCl_3,KCl$, were written by Werner thus:

$$[Pt(NH_3)_4]Cl_2 \qquad K[AuCl_4].$$

The four ammonia molecules or chlorine atoms were said to be co-ordinated to the central atom, whose co-ordination number was therefore 4. In $[Co(NH_3)_6]Cl_3$, the co-ordination number of cobalt is 6. The conception of the co-ordinate bond gives precision to these views. Indeed, since Werner's theory was advanced to explain the nature of compounds which were unaccounted for on older theories of valency, the same compounds may well form a crucial test of the newer theories of valency.

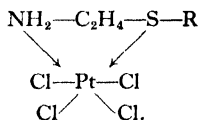
On these theories the structure of $KAuCl_4$ arises thus:

$$\begin{array}{c} :\ddot{Cl}: \\ :\ddot{Cl}:\ddot{Au} \\ :\ddot{Cl}: \end{array} + K^+[:\ddot{Cl}:]^- \qquad K^+\left[\begin{array}{c} :\ddot{Cl}: \\ :\ddot{Cl}:\ddot{Au}:\ddot{Cl}: \\ :\ddot{Cl}: \end{array}\right]^- .$$

Here the chloride ion supplies the two electrons required to complete the octet of the gold atom. Using bond symbols, the complex molecule $CoCl_3, 3NH_3$ may be represented thus:

$$\left[\begin{array}{c} Cl \searrow \quad \swarrow NH_3 \\ Cl - Co \leftarrow NH_3 \\ Cl \nearrow \quad \nwarrow NH_3 \end{array}\right]^0 .$$

It will be useful to give here a few examples of Werner's formulæ, and contrast them with the ordinary formulæ.

$Cr_2(SO_4)_3, 6H_2O$	$[Cr_2(OH_2)_6](SO_4)_3$
$K_2SnO_3, 3H_2O$	$K_2[Sn(OH)_6]$
$K_2PtO_3, 3H_2O$	$K_2[Pt(OH)_6]$
K_2PtCl_6	$K_2[PtCl_6]$
$FeCl_3, 6H_2O$	$[Fe(OH_2)_6]Cl_3$

Modern stereo-chemical theory recognizes that the atoms, molecules, or radicles within the bracket have a very definite space relationship to the central atom. The group AX_4 will have the X atoms more or less at the points of a tetrahedron, the A atom occupying a central position. In some cases the atoms may be co-planar, the X atoms then occupying the corners of a square. In the group AX_6, the X atoms occupy the points of a regular octahedron. Atoms, such as Cl, which are outside these inner groupings exhibit their normal ionic reactions, in contrast to those within the complex.

Such association of parts might conceivably arise from mutual attraction of molecules which are dipoles, as indeed NH_3 and H_2O are. Such cases do exist. However, many cases of optical activity associated with both tetrahedral and octahedral symmetry are known and this involves definite, directed valency bonds. In 1930, Mann found that the undernoted co-ordination derivative of $PtCl_4$ formed optically active isomers, the separate molecules being inactive. The formula, somewhat simplified, is

```
NH₂—C₂H₄—S—R
   ↘       ↙
   Cl—Pt—Cl
   Cl/   \Cl.
```

This must mean that co-ordination has produced an asymmetric centre in the sulphur atom, which is now akin to the sulphur in the sulphinic ester mentioned above. Hence there must be a definite link between sulphur and platinum.

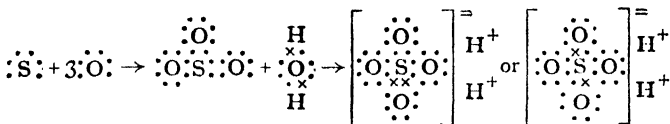
An outstanding application of the co-ordinate link appears

in the structures assigned to the acid radicles, $[AO_4]^n$, where A may be S, Se, Cr, Mn, P, Si, etc.

For formal presentation, many of these acids are represented in this book by formulæ such as $OX(OH)_3$ and $O_2X(OH)_2$, but these are scarcely justifiable as constitutional formulæ. The formula $SO_2(OH)_2$ for sulphuric acid, which, when expanded becomes

$$\begin{matrix} O & & O-H \\ & \gg S \lessdot & \\ O & & O-H \end{matrix}$$

, suggests that there are two ways in which the oxygen atoms are attached to sulphur, whereas there is no reason to believe that such is the case in the sulphate ion, at least in the sense which this formula suggests. The following is the manner in which the atoms in the sulphate ion are put together, two extra electrons (shown ×) being derived from the two hydrogen atoms of water, which thus become ions:

$$:\ddot{S}: + 3\,:\ddot{O}: \rightarrow \begin{matrix} :\ddot{O}: \\ :\ddot{O}:\ddot{S}::\ddot{O}: \end{matrix} + \begin{matrix} H \\ :\ddot{O}: \\ H \end{matrix} \rightarrow \left[\begin{matrix} :\ddot{O}: \\ :\ddot{O}:\ddot{S}:\ddot{O}: \\ :\ddot{O}: \end{matrix}\right]^{=} \begin{matrix} H^+ \\ H^+ \end{matrix} \text{ or } \left[\begin{matrix} :\ddot{O}: \\ :\ddot{O}:\ddot{S}:\ddot{O}: \\ :\ddot{O}: \end{matrix}\right]^{=} \begin{matrix} H^+ \\ H^+ \end{matrix}$$

Combination of SO_3 with water involves the opening out of the double bond (: :), but although one, or perhaps two, oxygen atoms are attached to sulphur wholly or partly by borrowed electrons (× ×), it cannot be supposed that this kind of bond, when formed, is distinguishable from the other, or that when water is removed from H_2SO_4 it is necessarily the same oxygen atom which breaks away in company with hydrogen.

The reason for the non-existence of H_4SO_5 and H_6SO_6 is that the sulphur atom cannot accommodate more than four oxygen atoms. The existence of hydrates such as H_2SO_4,H_2O and $H_2SO_4,4H_2O$ is quite another matter, and it will be seen shortly how the sulphate ion can become hydrated.

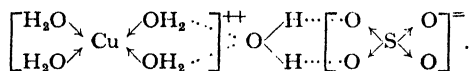
In the general formula, $[AO_4]^n$, therefore, *n* signifies the number of electrons to be borrowed from outside to supply

A with a completed octet: this number varies with the number of valency electrons possessed by A. Such acids in the undissociated and dissociated states may be written thus:

$$\begin{matrix} HO \searrow & & \nearrow O \\ & Cl & \\ O \swarrow & & \searrow O \end{matrix} \qquad \left[\begin{matrix} O \nwarrow & & \nearrow O \\ & Cl & \\ O \swarrow & & \searrow O \end{matrix}\right]^{-} H^{+}.$$

Water of Crystallization.—It was a conspicuous merit of Werner's structural theory that it gave definite positions to molecules of water or of ammonia in hydrates and ammoniates.

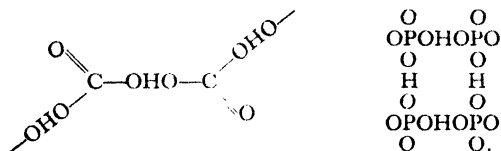
Cupric sulphate, $CuSO_4$, $5H_2O$, forms the monohydrate, $CuSO_4$, H_2O, at 100°: stronger heating liberates SO_3 before all the water is lost. Hence a differentiation of the water present may be assumed. It is significant that $CuSO_4$, $4NH_3$, H_2O is formed in presence of water, whilst $CuSO_4$, $5NH_3$ is formed under anhydrous conditions, and in the presence of water exchanges one NH_3 for one H_2O molecule. The pentahydrate may be written thus: $[Cu(H_2O)_4]$ $[SO_4, H_2O]$, and from crystal analysis it appears to have the structure:

$$\left[\begin{matrix} H_2O \searrow & & \swarrow OH_2 \cdots \\ & Cu & \\ H_2O \nearrow & & \nwarrow OH_2 \cdots \end{matrix}\right]^{++} \vdots\, O \begin{matrix} \diagup H \cdots \\ \diagdown H \cdots \end{matrix} \left[\begin{matrix} \cdot O \nwarrow & & \nearrow O \\ & S & \\ \cdot O \swarrow & & \searrow O \end{matrix}\right]^{=}.$$

Four H_2O molecules are co-ordinated to the cupric ion, all being in one plane, while the fifth H_2O forms a link between the complex cation and the tetrahedral sulphate ion.

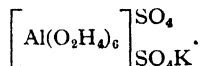
The hydrogen atoms were formerly considered to be linked co-ordinately to oxygen, thus: —O—H←O—, but this involves bivalent hydrogen with four electrons, which is difficult to interpret theoretically. Here the structure O—H···O marks a connection between the atoms which is not yet fully explained. On modern theories of crystal structure, the oxygen atoms of $SO_4^{=}$ are considered each to possess some negative charge (see also silicates): indeed this may be implied in the structure, O←S, which is equivalent to Lowry's semi-polar double bond. Hence the hydrogen may be held to one oxygen atom by electrostatic forces, the two atoms so bridged or bonded being drawn closer together.

The existence of such hydrogen " bridges " is well authenticated in crystal chemistry. Thus, the compound, KHF_2, is considered to be K[FHF] and the same link is present in the solids, $Na[HCO_3]$ and $K[H_2PO_4]$:

```
O            OHO
  \\        /
   C—OHO—C
  /         \\
OHO           O
```

```
O    O
OPOHOPO
O    O
H    H
O    O
OPOHOPO
O    O.
```

The negative ionic charges are neutralized by the positive ions Na^+ and K^+ suitably disposed in the crystal structure.

An alum such as K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$ was formulated by Werner thus:

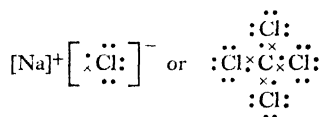
$$\left[Al(O_2H_4)_6\right]\begin{matrix}SO_4\\SO_4K\end{matrix}.$$

According to the work of Lipson (1935), polymerization of H_2O to give (H_4O_2) is not to be assumed. For every six molecules of water which are co-ordinated octahedrally to one Al atom, there are six others which serve to bind the $[Al(H_2O)_6]^{+++}$ octahedra, the sulphate, and the potassium ions in the crystalline structure. It is evident that molecules of water may play two rôles in structural chemistry. Even methane and the inert gases form solid hydrates, attributable to weak van der Waals forces.

Valency Number.—The older definition of valency as the combining capacity of an atom, or as the ratio

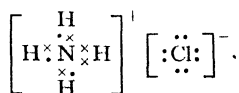
$$\frac{\text{atomic weight}}{\text{equivalent weight}},$$

leads us to inquire if it is now possible to provide a simple rule whereby the variations of this property may be expressed as numbers. No simple rule exists, for atomic linkings can arise in various ways. Grimm and Sommerfeld proposed (1925) that the valency of an atom is given by the number of its electrons used to effect union with other atoms. This for

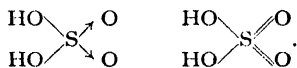
the most part satisfies definitely ionized or purely covalent compounds such as:

$$[Na]^+\left[\,\overset{\times}{.}\ddot{\underset{..}{Cl}}:\,\right]^- \quad \text{or} \quad \begin{array}{c} :\ddot{Cl}: \\ :\ddot{\underset{..}{Cl}}\,\overset{\times}{.}\,\underset{\times .}{\overset{. \times}{C}}\,\overset{.}{\times}\,\ddot{\underset{..}{Cl}}: \\ :\underset{..}{Cl}: \end{array}$$

Here sodium and chlorine are univalent since one electron has passed from sodium to chlorine, and in CCl_4 carbon is quadrivalent having provided four electrons for its union with four chlorine atoms.

Difficulties arise when co-ordinate links are present. Ammonium chloride is

$$\left[\begin{array}{c} H \\ H\overset{\times}{.}\underset{\times .}{\overset{. \times}{N}}\overset{\times}{\times}H \\ H \end{array}\right]^+ \left[:\ddot{\underset{..}{Cl}}:\right]^- .$$

and, on Grimm and Sommerfeld's rule, nitrogen may be said to be quinquivalent, since the formation of ammonium chloride requires nitrogen to utilize its five electrons. Nevertheless the structure of the ion $[NH_4]^+$ is better defined if nitrogen be called 4-covalent, for there is no reason to suppose that the co-ordinate link, once formed, differs from the other links present. The rule makes platinum quadrivalent in $PtCl_4$ and $[PtCl_6]^{=}$, though in the complex ion platinum is better described as being 6-covalent.

Sulphuric acid has been formulated in two ways, thus:

$$\begin{array}{c} HO \diagdown \quad \nearrow O \\ S \\ HO \diagup \quad \searrow O \end{array} \qquad \begin{array}{c} HO \diagdown \quad /\!\!/ O \\ S \\ HO \diagup \quad \backslash\!\!\backslash O \end{array} .$$

Both structures, following the rule, give sulphur a valency of 6 in conformity with older ideas. The first correctly represents sulphur as being 4-covalent.

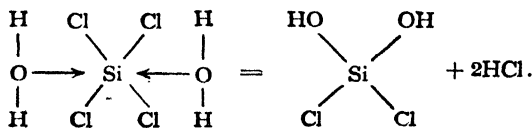
Covalencies Greater than Four.—Electrovalency and pure covalency are periodic in character, the value and type depending on the group position of the element which is decided by the number of electrons available for octet for-

mation. In some cases the octet rule breaks down. Thus, OsF_8, the only known octifluoride, vaporizes easily without dissociation and is therefore probably an 8-covalent compound in which 16 electrons bind the osmium atom to the fluorine atoms. The oxide OsO_4 is also volatile and is probably similarly constituted, each oxygen being linked to osmium by two covalent bonds. Alternatively, as in the second structure (which preserves the octet rule), the union may be by semipolar bonds, all the electrons being provided by the osmium atom.

```
      :O:                      ..
       ..                     :O:
 ..    ..    ..            ..  ..  ..
 O: :Os: :O               :O:Os:O:
 ..    ..    ..            ..  ..  ..
       ..                     :O:
      :O:                      ..
```

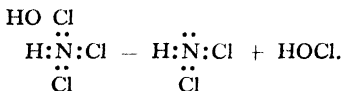
Many examples of complex ions are known where the octet has been increased by co-ordination. Thus in $[PtCl_6]^{=}$ and $[Co(NH_3)_6]Cl_3$, platinum and cobalt each possess 12 electrons in the valency shell. This display of higher covalency is not dependent on the group position of the element and is not periodic in character. According to Sidgwick, the maximum covalency which an element may show depends on its position in series. Thus for the series lithium to fluorine, the valency group may contain 8 shared electrons (4-covalency), from sodium to bromine, 12 shared electrons (6-covalency), and for succeeding elements, 16 shared electrons (8-covalency).

In support of these views Sidgwick points out that $SiCl_4$, but not CCl_4, is hydrolyzed by water, for the silicon atom can accommodate 12 electrons in the valency shell, and so react with water thus:

```
H   Cl    Cl   H        HO        OH
|     \   /    |          \      /
O ——→  Si  ←—— O    =       Si          + 2HCl.
|     /   \    |          /      \
H   Cl    Cl   H        Cl        Cl
```

By repetition the hydrolysis is completed. In CCl_4 the carbon

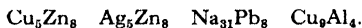
atom has already its maximum covalency of four, and so cannot react with water in this way. The inertness of SF_6 towards water may be attributed to the same cause, for sulphur has here its maximum covalency of 6, which cannot be increased by co-ordination of water molecules.

The hydrolysis of NCl_3 occurs because the water molecule may be attached through hydrogen to the lone electron pair of nitrogen. Hypochlorous acid is then formed, thus:

$$\begin{array}{c}\text{HO Cl} \\ \text{H}:\ddot{\underset{\cdot\cdot}{\text{N}}}:\text{Cl} \\ \text{Cl}\end{array} = \begin{array}{c}\\ \text{H}:\ddot{\underset{\cdot\cdot}{\text{N}}}:\text{Cl} \\ \text{Cl}\end{array} + \text{HOCl}.$$

Two repetitions of the process produce ammonia.

It may be observed here that Sugden, on the basis of parachor measurements, makes considerable use of single electron links in place of the duplets of covalency, and is thus enabled to maintain the octet in atomic structures. (See the hydrides of boron and PCl_5).

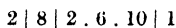
Metallic Links.—Simple valency relationships break down completely in most intermetallic compounds such as may be present in alloys. Metallic properties such as electrical conductivity and reflection of light require the presence of electrons which have some freedom of movement in the structure, so that the metallic link must be somewhat different from the links in organic and inorganic compounds where all the valency electrons form stable groupings. The compounds below, which possess the same lattice structure, illustrate these abnormal valency relationships.

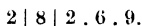
$$Cu_5Zn_8 \quad Ag_5Zn_8 \quad Na_{31}Pb_8 \quad Cu_9Al_4.$$

It appears to be significant for the particular structure that the ratio of the total number of valency electrons to the number of atoms is 21/13 in each case.

Polyvalency.—The notable polyvalency shown by transition elements in the wider sense is due to their ability to withdraw valency electrons from their inner groups. These changes may occur in single units, as with manganese, which

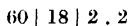
may show valencies of 1, 2, 3, 4, 6 and 7. The behaviour of manganese is dealt with under oxidation; meantime, the cuprous and cupric states of copper may be used in illustration.

Copper occurs at the end of the first transition series and has the electron structure:

2 | 8 | 2 . 6 . 10 | 1

Cuprous salts arise when the single valency electron is removed, and thus resemble the alkali salts. Cupric salts require an additional electron from the next group giving the cupric ion Cu^{++} the structure:

2 | 8 | 2 . 6 . 9.

Polyvalency of another type appears in later elements of the first two short periods. The sulphur atom in $SO_3^{=}$ is considered to have an octet of electrons, only three pairs, however, being used to bond the three oxygen atoms. Co-ordination of one oxygen atom to the lone pair produces sulphate ion, $SO_4^{=}$, and in this oxidation the inner electron groups of sulphur remain untouched. On older ideas the sulphur valency changes from 4 to 6, but the change is more aptly described as from 3- to 4-covalency. The formation of $[NH_4]^+$ from NH_3 is similar and the oxyacids of chlorine furnish another example (see Chap. IV).

Sidgwick has pointed out that the heavier elements in B sub-groups exhibit varying valency for yet another reason, namely the tendency of a pair of electrons to become " inert ". This is marked in the series, Hg, Tl, Pb, Bi. The structure of the lead atom, for example, is

60 | 18 | 2 . 2

and the production of Pb^{++} involves removal of two valency electrons, leaving a pair which are inert and behave like the helium pair of electrons, just as the octet confers something of the stability of argon.

The stable mercury atom is

60 | 18 | 2

and mercuric compounds result when the two valency electrons are utilized. Mercurous mercury is, however, $[Hg\text{-}Hg]^{++}$, two of the four available electrons bonding two atoms into a bivalent complex.

Colour in Inorganic Compounds.—The exact relationship between colour and constitution in inorganic compounds is not known, but it seems to correspond in the main to a looseness or an unsaturation in the electronic structures. Lewis pointed out that the molecules NO, NO_2, and ClO_2 were odd in that they contained 11, 17 and 19 electrons respectively. The last two are coloured, though when N_2O_4 is formed, the colour of NO_2 disappears. It is characteristic of the transition elements, with their facile interchange of electrons, that their compounds are coloured. Anhydrous cupric sulphate is white, though the hydrated or ammoniated cupric ion is coloured. This in part is attributed by Fajans to a constraint or deformation of the electron systems of the co-ordinated molecules.

Cobaltous chloride combines with 1, 2, or 6 H_2O. The change in colour of the hydrated salt from red to blue by heating or the addition of alcohol has generally been attributed to dehydration; but there is reason to believe that complex anions are formed thus:

$$CoCl_2 \rightleftharpoons Co^{\cdot\cdot} + 2Cl'; \qquad CoCl_2 + 2Cl' \rightleftharpoons [CoCl_4]''.$$

When, e.g. sufficient concentrated hydrochloric acid is added to a pink solution of cobaltous chloride the colour becomes blue, and there is evidence that a blue anion $CoCl_3'$ or $CoCl_4''$ is formed. Nevertheless rise of temperature converts a solution of cobaltous chloride containing hydrogen chloride from pink to blue, and this is attributable to dehydration.

Anhydrous cupric chloride is brown, and with a little water yields a brown solution which on progressive dilution becomes green and eventually blue, the colour of the hydrated cupric ion. Hydration plays a part in these changes, though in con-

centrated solution the complex $[CuCl_4]^{--}$ is believed to exist.

Magnetic Properties of Atoms.—The rotation of electrons in orbits will constitute elementary magnets which may or may not be neutralized by reason of their arrangement within the atom. An external magnetic field will distinguish the two types, for, should the atoms possess a resultant magnetic moment, the magnetization induced will be in the same sense as the external field, and the substance is *paramagnetic.* On the other hand, for a substance whose atoms have zero moment, the magnetization will be in the opposite direction to the field. Such substances are *diamagnetic*, as all substances are, but diamagnetism may be overshadowed by paramagnetism when such exists.

The inert gases are diamagnetic since their electron groups and sub-groups are completed. Paramagnetism is associated with incomplete groups such as are found in the ions of transition elements.

The complex salts, $K_4[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ are diamagnetic, the central atoms Fe and Co, possessing the same total number of electrons (36) as the inert gas krypton.

Paramagnetism appears in $K_3[Fe(CN)_6]$ and $[Cr(H_2O)_6]Cl_3$, since the atoms of Fe and Cr are one and three electrons, respectively, short of the atomic number of krypton.

CHEMICAL PROPERTIES

As a common criterion of the chemical characters of the elements, it may be well to employ their electro-chemical behaviour, as was done by Berzelius. Before, however, this can be done, it must be understood what is meant by the terms electro-positive and electro-negative, or, more simply, positive and negative, as applied to elements. It may be said that these terms are equivalent to the words metallic and non-metallic respectively. These latter expressions do not, however, convey any more definite meaning, when chemically considered, than the former ones.

Definite conceptions on this subject are derivable from the

theory of electrolytic dissociation. Zinc and copper may be contrasted in their tendency to pass into the ionic state in solution. Since metallic zinc displaces hydrogen from dilute sulphuric acid, whilst copper is without action upon this acid, zinc has a superior *solution pressure* to copper; and since cæsium reacts with water more vigorously than lithium, it, similarly, has a higher solution pressure than the latter element.

It is well known that this solution pressure of zinc expresses itself in the form of electro-motive force when solution of that metal takes place in a simple galvanic cell; and according to modern electro-chemical theories * the voltages which show the relative solution pressures of the metals are appropriately measured by the potential differences established between metals and their own salt solutions at molar dilution.

The following are a few of the values which have been thus observed; the sign shown is that assumed by the metal.

Mg	in $MgSO_4$	=	− 1·55	vo
Zn	,, $ZnSO_4$	=	− 0·76	,,
Cd	,, $CdSO_4$	=	− 0·40	,,
Fe	,, $FeSO_4$	=	− 0·44	,,
Cu	,, $CuSO_4$	=	+ 0·34	,,
Ag	,, Ag_2SO_4	=	+ 0·80	,,

Whilst exact values have not been obtained in all cases, the following is the order of electro-potential of the principal elements:

Metals: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Al, Cr, Mn, Zn, Fe, Cd, Tl, Co, Ni, Sn, Pb, H, Sb, Bi, As, Cu, Hg, Ag, Pd, Pt, Au, Ir, Rh, Os.

Non-metals: Si, C, B, N, Se, P, S, I, Br, Cl, O, F.

This order represents also, as regards the metals, the relative power of displacing other metals from salt solutions; so that any chosen metal can precipitate from solutions of equivalent strength any metals that follow it in the list.

The numerical values upon which the above series is based depend as regards the metals upon their tendency to pass into

* For which works on electro-chemistry may be consulted.

solution as basic ions. Thus the series illustrates what may be called the metallic reactivity of the metals, or their true electro-positiveness.

It is at once apparent, on consideration of this sequence, that *electro*-positiveness or metallic reactivity towards acids or salt solutions is not always the same thing as *chemical* positiveness or basic nature, as judged by the properties of oxides.

For example, whilst the alkali metals stand at the head of the list in both categories, arsenic and antimony, as shown by the properties of their oxides and other compounds, are less metallic—or more non-metallic—than copper or gold, although electrically they are more positive than these metals. Thus the electro-positive and base-producing properties of a metal are not always coextensive. Aluminium, for instance, is a powerfully electro-positive metal, but its base-producing properties are feeble. The term *basigenic* will be therefore employed when necessary to describe those characteristics of a metal which are expressed through the properties of its oxides and other compounds, and the term *acidigenic* will similarly be used to denote the acid-producing property of a non-metal.

For the present, however, the agreement rather than the difference between the electrical and chemical properties of an element may be considered. Mention may be made of the following connected properties:

(*a*) Power of mutual displacement and of combination under equivalent conditions.

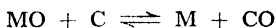
(*b*) Relative thermal effect of combination.

(*a*) From a compound of an element with an electro-negative atom or group, a more electro-positive element will displace a less electro-positive. Thus, as before shown, zinc, which is more electro-positive than copper or silver will displace these metals from solutions of their salts, whilst copper will displace silver from solutions of silver salts. And conversely, from a similar compound, a more electro-negative will displace a

less electro-negative element. For example, bromine will displace iodine, and chlorine will displace bromine and iodine from solutions of metallic iodides, and bromides and iodides respectively.

In general, combination will occur most readily between elements most widely separated in electro-chemical character, though this statement must be taken with certain limitations. The actual result of a chemical reaction will depend on the conditions obtaining in the reacting system, and in a self-contained system may be shown to follow the law of mass action.

Thus, if chlorine and bromine were in competition for combination with a given amount of a metal the actual amounts of chloride and bromide produced would depend on the relative active masses, that is, the number of equivalents per unit volume, of the competing elements, as well as upon their relative affinities; bromide might even preponderate in the product if bromine was originally present in considerable excess of chlorine, though a proper interpretation of the quantitative data would show that the affinity of the chlorine was superior. Again, many of the oxides of the metals are reduced by heating with the less positive carbon. Here it must be remembered that one of the products of reaction (oxide of carbon) is removed from the system as soon as it is formed, so that the reversible reaction

$$MO + C \rightleftharpoons M + CO$$

will proceed in the direction of the upper arrow to completion.

(*b*) Generally speaking, the thermal value of a reaction will be greatest when the uniting elements are most widely separated in chemical character. Thus the molecular heats of formation of the halogen acids are:

$$[H, F] = 389K, [H, Cl] = 220K, [H, Br] = 84K, [H, I] = -60K.$$

There is sometimes, as in the case of the alkali chlorides, not much difference in the heats of formation in a series. Laurie has shown that these heats of formation vary periodically.

Since combination is most likely to occur between elements widely separated in the chemical series, it appears that, of several possible reactions, that involving the greatest heat evolution may be expected to take place. This conclusion was expressed by Berthelot in his " law of maximum work " or " the necessity of reactions ", which asserted that " every chemical change accomplished without the addition of external energy tends to the formation of that body or system of bodies the production of which is accompanied by the development of the maximum quantity of heat ". This statement is open to criticism because it denies that a reversible chemical reaction can occur, whilst it is well known that many reactions may be reversed by altering the conditions of concentration and temperature of the reacting substances.

Thus endothermic reactions may take place at high temperature, contrary to the provision of Berthelot's law, though at absolute zero only exothermic changes occur, and the law then becomes true.

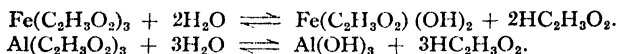
When, however, the thermal value of a particular reaction is large, and the temperature not high, that reaction will probably take place, but great care must be exercised in interpreting the thermal data of a reaction, and definite knowledge of its conditions is necessary.

Finally, some general points connected with the electrochemical character of elements may be referred to.

The most electro-positive are the most typically metallic elements; their oxides are basic, and their hydroxides soluble in water, and alkaline. They are the metals that produce true salts which are not decomposed by water and whose solutions are electrolytes.

Passing to the less electro-positive elements, oxides or hydroxides presenting a dual character are encountered, these being basic towards strong acids, and acidic towards strong bases. Of these, aluminium hydroxide, $Al(OH)_3$, is a good example. Such oxides or hydroxides form salts which are more or less readily acted on by water, yielding basic salts

or even the hydroxides by hydrolysis; thus ferric chloride and the acetates of iron and aluminium are all hydrolyzed.

$$Fe(C_2H_3O_2)_3 + 2H_2O \rightleftharpoons Fe(C_2H_3O_2)(OH)_2 + 2HC_2H_3O_2.$$
$$Al(C_2H_3O_2)_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HC_2H_3O_2.$$

With such metals, the character of the oxide is often determined by the proportion of oxygen present, that is, by the operative valency of the metal. Thus, while chromium forms the positive trivalent ion $Cr^{\cdot\cdot\cdot}$, sexivalent chromium appears as a constituent of the negative chromic acid ion CrO_4''.

Finally, the electro-negative elements whose oxides are acidic yield acids as hydroxides. Chlorides of these elements are not salts; they are in general distinguished by volatility, by the facts that they are not acted on by strong sulphuric acid, and that water decomposes them, yielding hydrochloric acid and the corresponding oxyacids of which they are the chloranhydrides.

It has been observed previously that electrovalent and covalent links are associated with the above distinctive properties of the molecules in which they are present. It has been explained also how ion formation (electro-valency) arises in elements which are near to an inert gas structure, electropositive elements reverting by loss, and electronegative elements advancing by gain of electrons to an inert gas structure in their ions. Atoms of electronegative nature unite by covalency. Nevertheless, many electropositive elements form covalent compounds and the conditions when electrovalency gives place to covalency must now be considered.

According to Fajans, two oppositely charged ions in close proximity will exert a mutual effect on the electron systems, for these are not rigid, but may be deformed or distorted to a degree depending on the charges and volumes of the ions. With great distortion the electrovalent link passes into covalency.

For simple negative ions, whose charges never exceed two, expansion of the electron system occurs in their formation,

so that the outer electrons are less under the control of the positive nucleus, being thus susceptible to distortion or even to removal to the extent required for covalency.

Positive ions of high charge and small volume exert a greater distorting effect on negative ions, with increased possibility of covalency. Indeed, a high charge can only be maintained if the ionic volume is high; with low volume the tendency to recapture electrons and form covalent links is great.

The conditions deciding which kind of valency may appear are summed up in *Fajans' Rules*:

Electrovalency	Covalency
Low positive charge.	High positive charge.
Large cation.	Small cation.
Small anion.	Large anion.

The table below shows the atomic volumes of the alkali metals and their atomic and ionic radii in Ångstrom units (Goldschmidt, 1926).

	Li	Na	K	Rb	Cs
At. Vol.	11·8	22·9	45·3	56·2	70·4
At. Rad.	1·56	1·86	2·23	2·36	2·55
Ion. Rad. M^+	0·78	0·96	1·33	1·49	1·65.

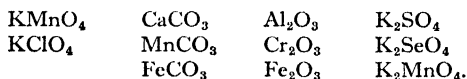
It will be observed that increase in magnitude follows increasing atomic number and electropositive character from lithium to cæsium; thus, all these values show an important connection with chemical properties.

In accordance with Fajans' rules electropositive character appears only in elements in lower valency states, though with a small anion it may be induced in higher valency states; thus SnF_4 is probably ionized but $SnCl_4$ is covalent. The weakly electropositive character of elements in sub-groups IB and IIB follows from their low atomic volumes. It follows also that co-ordination should occur most readily with smaller positive ions of high charge as, for example, in hydrates and ammines of the Werner type.

Ionic magnitudes are important in crystal structure; infor-

mation on this must be sought elsewhere. Nevertheless the results obtained from the X-ray analysis of solid structures are valuable for the light they shed on ionic and molecular constitution, and will be frequently used.

From time to time mention is made in this book of isomorphism illustrating similar valency and position of the structural units, as, for example, in the groups:

$KMnO_4$	$CaCO_3$	Al_2O_3	K_2SO_4
$KClO_4$	$MnCO_3$	Cr_2O_3	K_2SeO_4
	$FeCO_3$	Fe_2O_3	K_2MnO_4.

It is found, however, that isomorphous structures depend more on the radius ratio of the ions and the extent of their deformation or polarization by neighbouring atoms or groups, than on valency similarity. (See also Chap. I.)

When mixed crystals are formed the absolute size of the interchangeable units must correspond fairly closely.

The manner in which the chemical and electrical characteristics of the elements vary in the periodic classification may now be examined. The classification adopted in this book for the comparative study of the elements is that proposed by Mendeléeff, since it allows more ready comparison of elements which for valency reasons are found in the same group. Nevertheless the relationships of elements in series are important, and for these reference may be made to the extended table at the end of this book.

Variation in Periods.—Starting from the alkali metals, the change in the first two periods is regular from basigenic and electro-positive to acidigenic and electro-negative. In the first period (Series 2) lithium is the most electro-positive, fluorine the most electro-negative element, beryllium is less electro-positive than lithium and more electro-positive than boron, and so on.

Similarly with the second period, sodium to chlorine. At the end of each period there is an abrupt change from negative to positive—if the members of the helium group are ignored.

What is true for the first two short periods is also generally true for the succeeding long periods of seventeen elements; secondary periods are, however, discernible. A decrease in electro-positive character takes place from potassium through calcium and scandium to titanium and vanadium, which are somewhat electro-negative and acidigenic, their oxides yielding weak acids and their chlorides being volatile; chromium and manganese, and to a less extent iron, show a dual character, yielding both basic and acidic oxides; copper, though forming no acidic oxide, is less electro-positive than zinc, whose hydroxide nevertheless dissolves in alkalis. From gallium electro-negative and acidigenic characters increase through germanium, arsenic, and selenium to bromine. The elements of the two next long periods show similar relationships.

Each long period is characterized by the inclusion of a series of transition elements, each series ending with an element in Group VIII, or possibly with one of the elements comprising Group I B. The triads of Group VIII were formerly designated transition elements, but they really form part of these extended series.

It may be noted that transition elements possess high melting-points, the only other elements having comparable values being:

	Be	Si	C
M.P.	1278°	1458°	3800°.

Each transition element forms several oxides, the highest corresponding to the group valency (neglecting peroxides).

In the first long period the series:

Ti V Cr Mn Fe Co Ni

is characterized by the gradual emergence of stable bivalency and corresponding salts, maximum stability being shown in nickel.

Transition elements in the second and third long periods may display bivalency, but with more difficulty and not associated with saline character in the corresponding com-

pounds. Thus columbium, tantalum, molybdenum, and tungsten form "bivalent" chlorides of the type $(XCl_2)_3$. Normal bivalency appears in Group VIII elements.

In elements of the rare earths the dominant valency of three is associated with basigenic character.

It is to be noted that the members of the B sub-group are always less electro-positive than the corresponding members of the A sub-group. Thus zinc is less electro-positive than calcium, arsenic than vanadium, bromine than manganese.

Variation in Groups.—The variation in character from member to member of a group is perhaps one of the most valuable regularities revealed by the periodic classification, affording, as it does, the key to the systematic study of a group. This variation is from less to more electro-positive, with increase of atomic number in every group and sub-group with three exceptions, these being the eighth group, and sub-groups I B and II B. Thus in Group I A of the alkali metals, lithium is the least and cæsium the most electro-positive; and in Group VII B of the halogens, fluorine is the least and iodine the most electro-positive, or fluorine the most and iodine the least electro-negative.

The exceptional relationships of the elements of the eighth group and the sub-groups I B and II B are connected with the feeble reactivity of these elements and the corresponding ease with which they are separated from their compounds. And since this reactivity diminishes with increase in atomic number, so that the elements osmium, iridium, platinum, gold, and mercury are the most easily reducible of the metals, it follows that these metals are also among the most electro-negative; for, as before observed, metallic electro-negativeness, as indicated by position in the electro-potential series, is identical with metallic inertness. If gold is accepted as the most electro-negative metal, excepting Ir, Rh, and Os, sub-group I B being the sub-group in which metallic inertness is most highly developed, the relative positions of the six metals

Cu, Hg, Ag, Pd, Pt, Au

in the electro-potential series are not inconsistent with their positions in the periodic table.

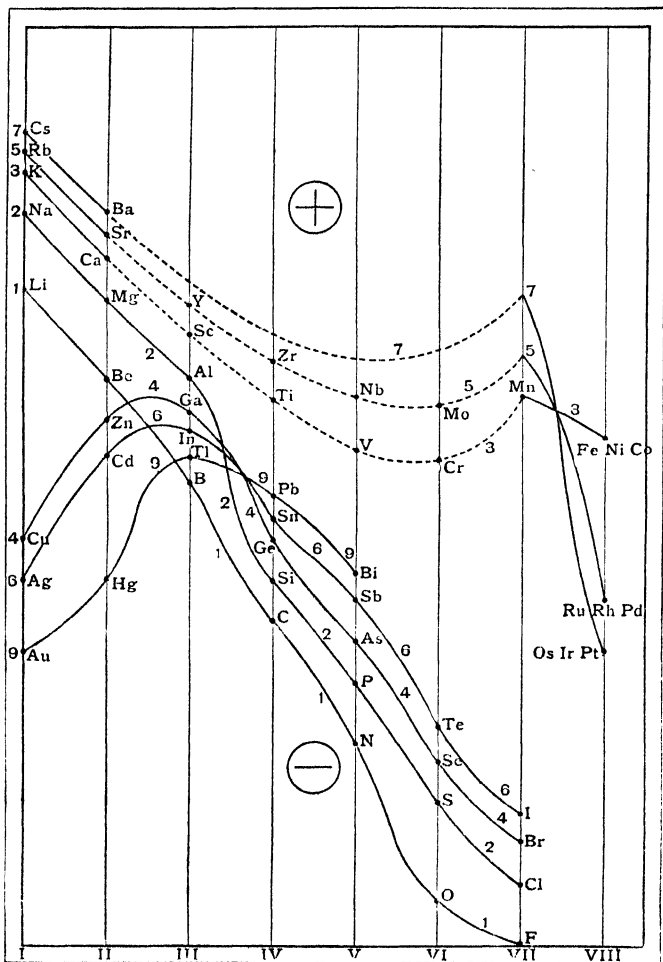
The diagram in Table II, constructed by Abegg,* shows approximately the periodic variation of electro-positiveness with atomic weight. The exceptional relationships of the elements of the eighth group are shown on the right after the intersection of the three upper curves, and those of the elements of Groups I B, II B, and possibly III B by the three ascending curves on the left, which, it will be observed, intersect before the fourth group is reached.

Thus there is in the periodic chart a region comprising Group VIII and sub-groups I B and II B, where chemical inertness and corresponding electro-negativeness are the chief characteristics, and these characteristics increase with rising atomic weight in these groups. When the chart (Table II) is on a cylinder this region is diametrically opposite to that occupied by the no-valency elements of the helium group.

The relationship of electro-positiveness to basigenic properties within these groups must however be discussed. It is within this region that the two properties appear not to be coextensive. Probably iron, cobalt, and nickel are more basigenic than the following elements of the eighth group, as they are more electro-positive; but whilst silver is more electro-negative than copper, it is nevertheless also more basigenic, since its oxide shows a faintly alkaline reaction with water, and its salts, in contradistinction to the cuprous salts, are stable towards water. But cadmium, although less electro-positive, is more basigenic than zinc, since its hydroxide is not dissolved by alkalis, and its salts are not so easily hydrolyzed as those of zinc.

It has been supposed that $Zn(OH)_2$ does not form a true compound with NaOH, but that alkali merely causes the $Zn(OH)_2$ to assume the colloidal state, and thereby aids the solution of zinc by water; nevertheless solid zincates have been obtained.

* *Zeit. anorg. Chem.* **39**, 367.

TABLE II

Gradation of Electro-Potential in the Periodic System. (After R. Abegg.) Copied by permission from *Zeit. anorg. Chem.*, **39**, 367.

It may further be observed that in all other groups but those just considered, the increase of basigenic—or electro-positive—properties is directly connected, as far as this is possible, with the loss of acid-producing, that is acidigenic, properties, this being particularly noticeable in the fifth group. In these exceptional sub-groups, however, there is no appreciable development of acidigenic with electro-negative properties; so that gold, one of the most electro-negative metals, does not form stable acids, whilst arsenic, which is far less electro-negative, is far more acidigenic, forming well-defined acids. Possibly a conflict between these two tendencies—the tendency towards chemical inertness with electro-negativeness, and the tendency towards acidigenic properties, also combined with electro-negativeness—may account for the anomalies noticed in these exceptional sub-groups, as, for example, in the case of cadmium and zinc.

From what has been said, it will now be seen that the diagonal drawn from lithium in the tabular arrangement, Group VIII being excluded, approximately divides the elements in such a way that those in the lower section are the more electro-positive or basigenic, and those in the upper section the more electro-negative or acidigenic in character; this being connected with the fact previously observed that the elements of the B or odd sub-groups are more electro-negative than their congeners in the A or even sub-groups.

Valency.—The maximum valency as shown in hydrogen, fluorine, chlorine, and oxygen compounds varies periodically.

Hydrogen Valency.—Hydrides are of three kinds: solid ionized hydrides of powerful metals, e.g. LiH, NaH, KH, CaH_2, BaH_2, which are decomposed by water, volatile hydrides of non-metals and metalloids, and the solid solutions or alloys formed by transition elements, including the rare earth elements. Boron and silicon form several and carbon many hydrides; boron appears to exceed the group-valency in its hydrides, e.g. B_2H_6, whose structure will be dealt with later. In Group IV the typical hydrides are CH_4, SiH_4, GeH_4. In

Group V there are NH_3, PH_3, AsH_3, SbH_3; in Group VI, OH_2, SH_2, SeH_2, TeH_2; and in Group VII, FH, ClH, BrH, IH.

Thus the hydrogen valency in the various groups is as follows:

Group	IV	V	VI	VII
	4	3	2	1;

clearly showing the periodic nature of this property.

The stability of the hydrides increases from IV to VII. This is not well shown by the hydrides of the non-metallic elements of Series 2, but is evident from a comparison of those of Series 3, SiH_4, PH_3, SH_2, ClH. This is in accordance with the development of non-metallic properties in passing along the series. In this connection it may be remarked that it is only the relatively non-metallic elements of the odd series, or the B sub-groups, in the long periods which form stable, volatile, alkyl compounds.

Halogen Valency.—In general fluorine realizes the highest valency of the element with which it is combined, and the fluorides are often more saline than the corresponding chlorides. This may be attributed to the small size of the fluoride ion.

The periodic nature of valency is aptly shown in the series, taken in group order:

$$LiF \quad BeF_2 \quad BF_3 \quad CF_4 \quad PF_5 \quad SF_6 \quad IF_7 \quad OsF_8$$

To the fluorides SF_6, IF_7 (and ReF_7), and OsF_8, there are no corresponding chlorides.

Chlorine Valency.—The highest chlorine compounds of the respective groups are represented by the following types:

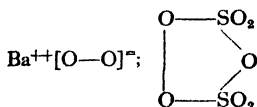
Group	I	II	III	IV	V	VI	VII	VIII
Type	XCl	XCl_2	XCl_3	XCl_4	XCl_5	XCl_6	XCl_5	XCl_4

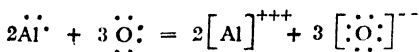
In Group V the form XCl_3 and not XCl_5 is the more stable; in Group VI the form XCl_6 is represented only by WCl_6, the type XCl_4 being more typical. In Group VII the form XCl_5 occurs only in $ReCl_5$, in Group VIII the tetrachloride is the

highest form, and in Group I the type XCl is departed from in $CuCl_2$ and $AuCl_3$. A periodicity nevertheless exists.

Iodides generally exhibit a lower valency than the group valency, hence the existence of TaI_5 is remarkable.

Oxygen Valency.—The term "oxygen valency" refers to that valency displayed in the highest typical oxide, by which must be understood the highest oxide in which each oxygen atom is united only to the nuclear atom or atoms of the second element; as distinguished from the peroxides of higher oxygen content, in which linkages of oxygen atoms to one another is found, as in BaO_2 and S_2O_7.

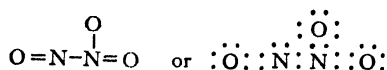
$$Ba^{++}[O\text{—}O]^{=}; \quad \begin{array}{l} O\text{——}SO_2 \\ | \qquad\quad \diagdown \\ | \qquad\qquad O \\ | \qquad\quad \diagup \\ O\text{——}SO_2 \end{array}$$

Oxides of the type X_2O_3, for example, are of at least two kinds: refractory metallic oxides, e.g. Al_2O_3, Cr_2O_3, Fe_2O_3, and volatile oxides of non-metals and metalloids, e.g. N_2O_3, P_2O_3, As_2O_3; whilst B_2O_3 and Bi_2O_3 appear to be intermediate in character between these two. The metallic oxides are probably formed by the exercise of electrovalency; i.e. by the transfer of electrons from the metal to oxygen, with the formation of ions thus, e.g.:

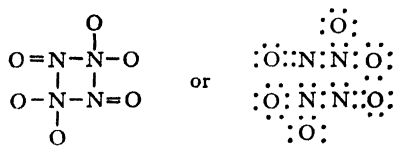
$$2\dot{\ddot{A}}\dot{l} + 3\,\ddot{\underset{\cdot\cdot}{O}}\!: \;=\; 2\left[Al\right]^{+++} + 3\left[:\!\ddot{\underset{\cdot\cdot}{O}}\!:\right]^{--}$$

Such oxides do not form molecules in the solid state, but, as revealed by X-ray crystal analysis, possess structures where oxygen atoms or ions are disposed spatially round the other atom. In Al_2O_3, for example, each Al atom has 6 oxygen atoms in octahedral disposition round it. This composite structure reduces to the empirical formula, Al_2O_3, which is a typical oxide and the expression of the tervalency of aluminium.

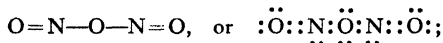
For comparison, consider the oxide N_2O_3 which volatilizes without decomposition when dry. This molecular formula

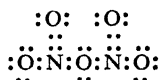
contains five atoms, which provide a total of $2 \times 5 + 3 \times 6 = 28$ electrons, since the N atoms provide 5, and the O atoms 6 electrons each. If, however, each atom were to be surrounded separately by an octet of electrons $5 \times 8 = 40$ electrons would be required. Consequently there must be in the molecule $\frac{40 - 28}{2} = 6$ bonds each consisting of a duplet of electrons.

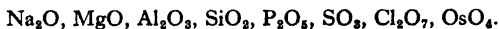
The formula may therefore be written:

```
     O                         ..
     |                        :O:
O=N—N=O     or    :Ö::N:N::Ö:
```

Such a formula, however, represents an unsaturated condition; and, as a matter of fact, the molecule of nitrous anhydride is N_4O_6, which may be represented thus:

```
       O                      ..
       |                     :O:
O=N—N—O               :Ö::N:N:Ö:
   |   |         or
O—N—N=O               :Ö:N:N::O:
   |                     :O:
   O                      ..
```

An alternative formula, which is perhaps preferable, because it does not represent contiguous nitrogen atoms, is:

```
O=N—O—N=O,   or   :Ö::N:Ö:N::Ö:;
```

In this case the double molecule may be constituted somewhat similarly. Indeed, the substance may be tautomeric and exist in the two forms; a certain mobility of structure being indicated by its blue colour. The nitrogen valency here is three, the group valency being five as in the typical oxide N_2O_5:

```
   :O:  :O:
    ..   ..
:Ö:N:Ö:N:Ö:
```

The following oxides, taken in group order, are typical:

Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, OsO_4.

Thus oxygen valency rises continuously from 1 to 8,

Group	I	II	III	IV	V	VI	VII	VIII
Oxygen valency	1	2	3	4	5	6	7	8,

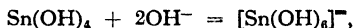
though from phosphorus onwards lower oxygen valencies likewise appear.

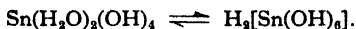
The degree of hydroxylation of which these oxides are capable is instructive.

Sodium and magnesium oxides form the hydroxides NaOH and $Mg(OH)_2$; the latter, however, is less stable than NaOH, being decomposed at a low red heat, and not being formed by direct combination of the oxide with water. $Al(OH)_3$ is more unstable than $Mg(OH)_2$, and loses water on exposure to the air; the aluminates, too, are chiefly meta-salts. $Si(OH)_4$ probably exists in dilute solution, and certain ortho-silicates corresponding to it are known; on decomposition it easily yields $SiO(OH)_2$ and $(SiO_2)_n$. $P(OH)_5$ is unknown, and the first anhydride, $PO(OH)_3$, easily loses water, forming $P_2O_3(OH)_4$ and $P_2O_4(OH)_2$, the latter of which, however, is stable at a red heat. $S(OH)_6$ and $SO(OH)_4$ are both unknown, and the meta-acid $SO_2(OH)_2$ is easily broken up into SO_3 and water.

The halogen oxyacids derived from X_2O_5 are monobasic, corresponding to $XO_2(OH)$, but salts corresponding to $IO(OH)_5$ are known. This higher hydroxylation is also shown by elements preceding iodine in the same period. Thus telluric acid is $Te(OH)_6$, potassium antimonate is $K[Sb(OH)_6]$, and potassium stannate is $K_2[Sn(OH)_6]$.

The highly hydroxylated stannate ion, for example, may arise from stannic hydroxide thus:

$$Sn(OH)_4 + 2OH^- = [Sn(OH)_6]^{=},$$

or it may be due to dissociation of two molecules of water of hydration which furnish the corresponding acid thus:

$$Sn(H_2O)_2(OH)_4 \rightleftharpoons H_2[Sn(OH)_6].$$

Lastly, OsO_4 appears incapable of direct hydroxylation, since its solution in water is neutral in reaction.

It will be observed that a gradation is manifested by these oxides as regards power of combining with water, and that, for atoms of low atomic number, the power of hydroxylation reaches a maximum with $Si(OH)_4$, and diminishes, like power of combining with hydrogen, through the fifth, sixth, and seventh groups to the eighth group. With atoms of higher atomic number, however, higher hydroxylation may occur.

CHAPTER III

OXIDES, HYDROXIDES, AND ALLIED COMPOUNDS

Oxides, or binary compounds of oxygen and other elements, are known for all elements except the inert gases.

On account of the universality of oxides, and of their simple relationships to the basic and acidic hydroxides, a study of the characteristics of the oxides of a group is of great value for comparative purposes.

In the periodic classification the typical oxide of the group is the highest oxide which displays basic or acidic character; for example, in Group II the oxides MO, corresponding with the salts MX_2, in Group VI the oxides MO_3, corresponding with the acids H_2MO_4, are the typical oxides. Higher oxides, such as MO_2 in Group II, and M_2O_7 in Group VI, are peroxides.

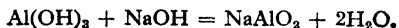
Oxides are classified in four main groups: *basic*, *acidic*, *neutral*, and *peroxides*.

Basic oxides differ in character according to the degree of electro-positiveness of the metal from which they are derived. The oxides of the most electro-positive elements, such as the alkali metals, are very stable, whilst those of the electro-negative metals, according to the electro-potential series, such as mercury, silver, and gold, are unstable, being easily decomposed by heat into metal and oxygen. The more strictly chemical differences, whose significance from the point of view of classification is greater, are shown in the manner of

formation and properties of the hydroxides, as will appear later.

Acidic oxides are formed by non-metallic elements, and their hydroxides are the oxyacids.

It must, however, be clearly understood that the terms basic and acidic are strictly relative. There is a class of oxides and hydroxides which exhibit both properties. These are the oxides of elements of ill-defined chemical property, which occur at transition points between basigenic and acidigenic elements in a series or group. As an example may be quoted the hydroxide of aluminium, which is soluble in caustic alkalis, and towards which it behaves as an acid; thus:

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$

Towards strong acids, however, it behaves as a base; thus:

$$Al(OH)_3 + 3HCl = AlCl_3 + 3HOH.$$

Such a salt as an aluminate easily suffers hydrolysis. Thus aluminic resembles silicic acid in not forming a stable ammonium salt, so that ammonium chloride added to a solution of aluminium hydroxide in alkali causes its precipitation. Zinc and chromic hydroxides dissolve in cold alkalis, but are reprecipitated on boiling. There is some doubt, moreover, whether salts are formed, since these hydroxides may assume the colloidal state, but in the latter case definite chromites exist to attest the acidic character of chromium sesquioxide.

Neutral oxides are such as form neither basic nor acidic hydroxides, nor yield such oxides by loss of oxygen. Water, carbon monoxide, nitrous and nitric oxides, are examples of such compounds. Carbon monoxide and nitrous oxide, however, are formed from formic and hyponitrous acids respectively, by loss of water, so that, although they do not unite with water to form these acids, their relation to them is such that they cannot be considered neutral oxides in the narrower sense.

Suboxides, such as Ag_4O and Pb_2O, may, however, be said to belong to this class, though not perhaps the tetroxides RuO_4 and OsO_4, which although yielding neutral solutions in water appear to form unstable compounds with alkalis.* The latter oxides may also be regarded as both acidic and basic peroxides, since they yield acidic and basic oxides by loss of oxygen.

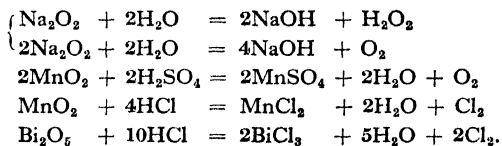
A *peroxide*, in the stricter sense, is an oxide containing more oxygen united to a certain quantity of an element than is contained in its highest typical oxide according to the periodic law. There are, therefore, *basic* and *acidic peroxides*. In this definition no account is taken of the various reactions in which an oxide may participate. For instance, manganese and lead dioxides, as well as bismuth pentoxide, are not peroxides in the sense of the definition, because their oxygen content does not exceed that of the typical oxides, which are Mn_2O_7, PbO_2, and Bi_2O_5 respectively. Na_2O_2, KO_2, BaO_2, S_2O_7 are, however, true peroxides. When, however, the first-mentioned oxides are attacked by acids, they form salts of the oxides MnO, PbO, and Bi_2O_3 respectively. Hence higher oxides than these and other salt-forming oxides are often considered to be basic peroxides.

Some typical reactions of basic peroxides are here set forth:

$$\begin{cases} Na_2O_2 + 2H_2O = 2NaOH + H_2O_2 \\ 2Na_2O_2 + 2H_2O = 4NaOH + O_2 \end{cases}$$

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

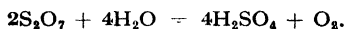
$$Bi_2O_5 + 10HCl = 2BiCl_3 + 5H_2O + 2Cl_2.$$

The reaction with hydrochloric acid is highly characteristic of peroxides, the amount of chlorine evolved being equivalent to the oxygen present in the peroxide in excess of that in the basic oxide corresponding to the salt formed. It may sometimes be assumed that a perchloride is first formed equivalent

* Tschugaev, *Compt. rend.* (1918), **167**, 162.

to the peroxide, and that this subsequently evolves chlorine. Such an assumption is only admissible when the higher chloride is known to exist.

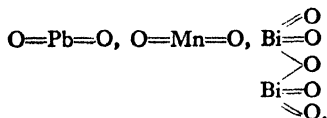
Another very general reaction of peroxides is the formation by them of salts corresponding to true basic oxides by direct union with lower acidic oxides. Sodium dioxide, when gently warmed in sulphur dioxide, burns, producing sulphate: $Na_2O_2 + SO_2 = Na_2SO_4$, and lead dioxide behaves similarly: $PbO_2 + SO_2 = PbSO_4$. In these reactions the peroxides behave as oxidizing agents. Such a property, however, is not in itself sufficient to justify the designation peroxide, for certain unstable oxides, such as Ag_2O, are oxidizing agents, though not peroxides.

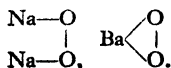
The properties of acidic peroxides are at first sight more complex, but are only apparently so. A true acidic peroxide is one, like the anhydride of perchromic or persulphuric acid, containing a higher oxygen content than the highest typical oxide of the group, so that by loss of oxygen in presence of water a typical acid is formed. Thus persulphuric anhydride readily decomposes with water in the following way:

$$2S_2O_7 + 4H_2O = 4H_2SO_4 + O_2.$$

Permanganic anhydride, Mn_2O_7, also yields a lower oxide, and oxygen, though not so readily as S_2O_7. It is not, however, a true acidic peroxide, because it is a typical oxide of the seventh group, and possesses normal properties as an acidic oxide; also, as will be seen later, its constitution differs essentially from that of S_2O_7. As indicated above, it might be considered to be a basic peroxide.

Mendeléeff has suggested a manner of classification of peroxides on structural grounds, depending on the valency of the element united to oxygen. The oxygen atom or atoms, over and above those required to form the basic oxide, may either be doubly linked to the metal atom or singly linked to the metal and to oxygen, forming a chain, and so preserving the valency of the metal in the basic oxide unchanged. The

dioxides of lead and manganese, and bismuth pentoxide, represent the first type, and are called *polyoxides*; thus:

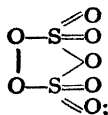
```
                            ⁄O
O=Pb=O, O=Mn=O, Bi=O
                             >O
                           Bi=O
                             \O.
```

The peroxides of the metals of Groups I A and II A and B conform to the second type, and are called *superoxides*. They are thus formulated:

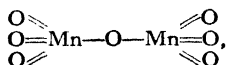
```
Na—O         /O
   |     Ba<  |
Na—O,        \O.
```

CLASSIFICATION

Group.		Basic.	Basic and Acidic.	Acidic.
I.	A.	Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O		
	B.	Cu_2O, CuO, Ag_2O, (AgO), Au_2O		
II.	A.	CaO, SrO, BaO		
	B.	MgO, ZnO, Cd_2O, CdO, Hg_2O, HgO	BeO, ZnO (?)	
III.	A.	Sc_2O_3, Y_2O_3, La_2O_3		
	B.	Tl_2O, Tl_2O_3	Al_2O_3, Ga_2O_3, In_2O_3	B_2O_3
IV.	A.	Ti_2O_2, Ti_2O_3, ZrO_2, Ce_2O_3, CeO_2, ThO_2	TiO_2	
	B.		GeO, SnO, PbO	(CO), CO_2, SiO_2, GeO_2, SnO_2, PbO_2
V.	A.	V_2O_2, V_2O_3	V_2O_4, V_2O_5	Cb_2O_5, Ta_2O_5
	B.	Bi_2O_3	Sb_2O_3	(N_2O), N_2O_3, NO_2,* N_2O_5, P_4O_6, PO_2,* P_4O_{10}, As_4O_6, As_2O_5, Sb_2O_5, (Bi_2O_5)
VI.	A.	CrO, MoO, Mo_2O_3, (WO_2), UO_2	Cr_2O_3, MoO_2, UO_2	CrO_3, MoO_3, WO_3
	B.			S_2O_3 (?), SO_2, SO_3, SeO_2, TeO_2, TeO_3
VII.	A.	MnO, Mn_2O_3		(MnO_2), MnO_3, Mn_2O_7
	B.			Cl_2O, ClO_2,* Cl_2O_7, I_2O_5, I_2O_7
VIII.		FeO, Fe_2O_3, CoO, Co_2O_3, NiO		$[FeO_3]$, CoO_2, NiO_2
		RuO, RhO, PdO	RuO_2, Rh_2O_3, RhO_2, PdO_2	$[RuO_3]$, $[Ru_2O_7]$, (RuO_4)
		OsO, $[IrO]$, PtO	Os_2O_3, OsO_2, Ir_2O_3, IrO_2, PtO_2	$[OsO_3]$, (OsO_4)

* Mixed anhydride   Oxides in round brackets () belong to more than one type.

Mendeléeff represented sulphur heptoxide, also, as a super-oxide—

$$\begin{array}{l} \qquad\quad \nearrow O \\ O-S=O \\ | \qquad > O \\ O-S=O \\ \qquad\quad \searrow O; \end{array}$$

but manganese heptoxide as a polyoxide, thus:

$$\begin{array}{l} O\searrow \qquad\qquad\qquad\quad \nearrow O \\ O=Mn-O-Mn=O, \\ O\nearrow \qquad\qquad\qquad\quad \searrow O \end{array}$$

since it does not contain an oxygen chain.

It will be observed that the true basic and acidic peroxides

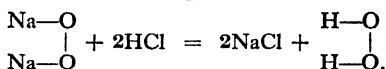
OF OXIDES

Neutral.	Suboxides.	Saline.	PEROXIDES.		
			Basic.	Acidic.	Neut.
H_2O			Na_2O_2, KO_2		H_2O_2
	Cu_4O, Ag_4O	Au_2O_2	(AgO)		
			CaO_2, SrO_2, BaO_2		
			{ MgO_2, CdO_2, ZnO_2		
			{ TiO_3, ZrO_3, CeO_3, Th_2O_7		
(CO)	Pb_2O	Pb_2O_3, Pb_3O_4		$[SnO_3]$	
{ V_2O, Cb_2O_2, Cb_2O_4, Ta_2O_4					
(N_2O), NO		Sb_2O_4, Bi_2O_4	(Bi_2O_5)		
(WO_2)		{ CrO_2, Mo_3O_8, W_3O_8, U_3O_8 }		CrO_4, UO_4	
TeO				CrO_5, S_2O_7	
		$Mn_3O_4(MnO_2)$	(MnO_2)		
		Fe_3O_4, Co_3O_4	Ni_2O_3		
(RuO_4)	Pd_2O				
(OsO_4)					

Oxides in square brackets [] do not exist, but their derivatives are known.

are superoxides, whilst those normal acidic oxides which behave as oxidizing agents are polyoxides.

A mode of distinguishing between the two classes is to be found in their behaviour towards an excess of water or dilute acid. A superoxide containing the group $\begin{matrix} -O \\ | \\ -O \end{matrix}$ yields hydrogen peroxide as a characteristic product, thus:

$$\begin{matrix} Na-O \\ | \\ Na-O \end{matrix} + 2HCl = 2NaCl + \begin{matrix} H-O \\ | \\ H-O. \end{matrix}$$

A polyoxide, however, like lead or manganese dioxide, is usually not attacked by dilute acids; with strong sulphuric or hydrochloric acid oxygen or chlorine is evolved, though of course the same is true of the action of a strong acid on a superoxide.

The mechanism of the evolution of oxygen or chlorine is, however, probably different in the two cases.

With a polyoxide, e.g. MnO_2, and strong H_2SO_4 or HCl, the following reactions take place:

$$2O{=}Mn{=}O + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

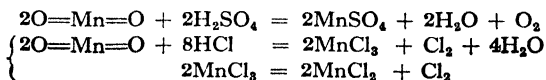
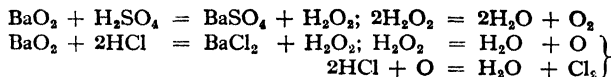
$$\begin{cases} 2O{=}Mn{=}O + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O \\ 2MnCl_3 = 2MnCl_2 + Cl_2 \end{cases}$$

or

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O;$$

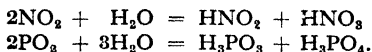
and with a superoxide

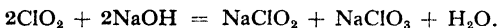
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2;\ 2H_2O_2 = 2H_2O + O_2$$

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2;\ \left.\begin{matrix} H_2O_2 = H_2O + O \\ 2HCl + O = H_2O + Cl_2 \end{matrix}\right\}$$

The well-known methods for the preparation of hydrogen peroxide depend, therefore, upon the employment of superoxides, under conditions of temperature and dilution that preclude the decomposition of the peroxide.

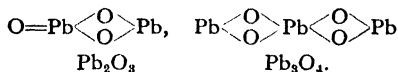
In addition to the above classes of oxides, certain compound oxides are known which are either *mixed anhydrides* or *salts.* Mixed anhydrides are acidic oxides which give rise to two acids when they react with water. Such oxides are NO_2 and

$(PO_2)_n$, which produce nitrous and nitric acids, and phosphorous and phosphoric acids thus:

$$2NO_2 + H_2O = HNO_2 + HNO_3$$
$$2PO_2 + 3H_2O = H_3PO_3 + H_3PO_4.$$

ClO_2, also, is of the nature of a mixed anhydride, which, though not reacting with water, gives chlorite and chlorate with alkali:

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O.$$

Oxides which are salts are compounds of basic and acidic oxides of the same metal.

Pb_2O_3 and Pb_3O_4 are respectively $PbO{\cdot}PbO_2$ and $2PbO{\cdot}PbO_2$, or lead meta- and lead ortho-plumbate:

$$\underset{Pb_2O_3}{O{=}Pb{<}^{O}_{O}{>}Pb}, \quad \underset{Pb_3O_4.}{Pb{<}^{O}_{O}{>}Pb{<}^{O}_{O}{>}Pb}$$

Other examples of this kind are known. They all illustrate the superior acidity of the higher over the lower oxide of a metal, which results in combination between relatively basic and acidic oxides with formation of a salt.

The facts discussed in the above paragraphs are set forth in the scheme of classification of oxides on pp. 110, 111.

HYDROXIDES

Hydroxides are compounds of oxides with water, formed by the appropriation of the elements of water in the following manner:

$$MO + H{-}OH \rightarrow M(OH)_2.$$

The reaction may be reversible with rise of temperature, the degree of reversibility determining the stability and definiteness of the hydroxide.

Definite hydroxides are to be found amongst the elements of the extreme groups, which possess marked basigenic or

acidigenic characters. It is these hydroxides which are capable of isolation in the free state, and which display the greatest stability when heated. The oxides of the alkali metals, for instance, readily combine with and powerfully retain water, with which they form hydroxides freely soluble in water. The oxides of the alkaline earth metals form hydroxides which are less stable than those of the alkali metals, and which retain their water less tenaciously. Magnesium hydroxide is not formed from the oxide by obvious slaking; it is slightly soluble in water, giving an alkaline reaction. The hydroxides of such metals as iron and zinc are not formed directly from the oxides, which are practically insoluble in water and give no alkaline reaction. These hydroxides may, however, be obtained by precipitation, and the basic properties both of the oxides and hydroxides are shown by their power of dissolving in and neutralizing acids.

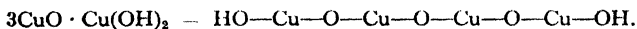
On passing to the non-metallic elements, chemical activity of the oxides and stability of the hydroxides are again met with. Oxides of these elements slake with or are soluble in water, forming hydroxides whose solutions are acid.

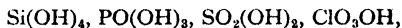
Thus the hydroxides of Groups I A and II A are alkalis, that is, they are strong bases, soluble in water; whilst the hydroxides of Groups VII B, VI B, and V B are the strong oxyacids.

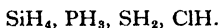
The hydroxide corresponding to an oxide MO_n is theoretically $M(OH)_{2n}$, each doubly linked oxygen atom being represented by two OH groups. With basic oxides this maximum hydroxylation is usually realized; thus the oxides Li_2O, BaO, Al_2O_3 correspond with the hydroxides $LiOH$, $Ba(OH)_2$, $Al(OH)_3$. Hydroxides of the central members of series of the periodic classification are unstable, especially those of the heavy metals of the eighth group and of silver, gold, and mercury. In some cases intermediate stages of hydroxylation are known. Aluminium hydroxide, for instance, easily loses water in the following stages:

$$Al(OH)_3 \longrightarrow Al_2O(OH)_4 \longrightarrow Al_2O_2(OH)_2 \longrightarrow Al_2O_3;$$

and cupric hydroxide, $Cu(OH)_2$, passes readily on warming in water into

$$3CuO \cdot Cu(OH)_2 = HO{-}Cu{-}O{-}Cu{-}O{-}Cu{-}O{-}Cu{-}OH.$$

Hydroxylation of an acidic oxide is seldom complete. The theoretically possible basicity of the acid corresponding to the oxide M_2O_3 is three; to the oxide MO_2 is four; and so on. But, just as the maximum number of hydrogen atoms which can combine with an element is four, so, with one or two exceptions, the maximum basicity of an acid, as measured by the number of hydroxyl groups combined with a non-metallic element, appears to be four. Tetrabasic silicic acid is known to exist, but it is very unstable, and proceeding in series the following are typical acids:

$$Si(OH)_4, PO(OH)_3, SO_2(OH)_2, ClO_3OH,$$

which correspond with the hydrides

$$SiH_4, PH_3, SH_2, ClH.$$

Definite exceptions to this rule are furnished by periodic acid, $IO(OH)_5$, and by telluric acid, $Te(OH)_6$. That iodine forms such a compound, rather than the other halogens, suggests that power of hydroxylation increases with increase of electro-positiveness in a negative group. Confirmation of this idea is found in the case of carbon and silicon, neither $C(OH)_4$ nor any of its inorganic derivatives being known. The non-existence of $NO(OH)_3$, as compared with $PO(OH)_3$, further illustrates this point. It must be observed, however, that the power of hydroxylation of a carbon atom is increased by the proximity of negative groups. For whilst $H_2C(OH)_2$ does not exist, $OC(OH)_2$ does, though it is unstable; and whilst $CH_3 \cdot CH(OH)_2$ is unknown, $CCl_3 \cdot CHO$ combines with water, forming $CCl_3 \cdot CH(OH)_2$. In the case of sulphur the basic salts $Pb_2SO_5(=PbO, PbSO_4)$ and $Hg_3SO_6(=2HgO, HgSO_4)$ exist; and they may be supposed to be related to $SO(OH)_4$ and $S(OH)_6$; but, inasmuch as they are not directly produced from sulphuric acid, there is no evidence of the existence of

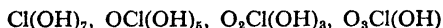
the above forms of the acid, although the hydrates H_2SO_4, H_2O and H_2SO_4, $2H_2O$ are known.

It may be observed that whilst hydroxylation is reduced to its lowest limits in the monobasic oxyacids of the seventh group, in the case of the typical oxides of the eighth group it is non-existent; osmium tetroxide, for example, seems incapable of hydroxylation and therefore possesses no acidic properties.

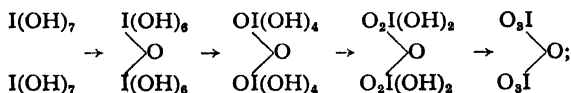
In strict nomenclature the term *ortho-* should be reserved for the fully hydroxylated form of an acid. In practice it has been found convenient to apply it to the most highly hydroxylated salt-forming type. The relationships between the several acids derivable from a single anhydride are best developed by tracing their formation from the hypothetical fully-hydroxylated type by loss of water. Phosphoric anhydride should theoretically give $P(OH)_5$ as the true ortho-acid; the highest known acid is $PO(OH)_3$, and this is consequently known as orthophosphoric acid; it is intermediate between the true ortho-acid and metaphosphoric acid; thus:

$$P(OH)_5 \rightarrow OP(OH)_3 \rightarrow O_2P(OH).$$

Similarly the series

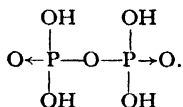
$$Cl(OH)_7,\ OCl(OH)_5,\ O_2Cl(OH)_3,\ O_3Cl(OH)$$

shows perchloric acid to be in reality the third meta-acid, derived from hypothetical $Cl(OH)_7$. As seen above, the compound $OI(OH)_5$ exists.

The term *pyro-* or *anhydro-* usually refers to the type of acid which results from dehydration of two or more molecules of the true ortho- or any intermediate form down to the meta-acid. Thus from $I(OH)_7$ the following series of acids may be derived:

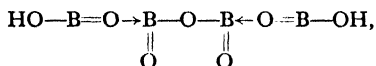
$$\begin{matrix} I(OH)_7 & & I(OH)_6 & & OI(OH)_4 & & O_2I(OH)_2 & & O_3I \\ & \rightarrow & \quad\rangle O & \rightarrow & \quad\rangle O & \rightarrow & \quad\rangle O & \rightarrow & \quad\rangle O; \\ I(OH)_7 & & I(OH)_6 & & OI(OH)_4 & & O_2I(OH)_2 & & O_3I \end{matrix}$$

the anhydride at last resulting.

Derivatives of numerous types of periodic acid are known, containing one or two iodine atoms per molecule.

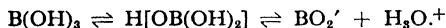
Pyrophosphoric acid $H_4P_2O_7$ is the best-known acid of this class, its constitution probably being:

$$\begin{array}{ccccccc} & & OH & & OH & & \\ & & | & & | & & \\ O & \leftarrow & P & -O- & P & \rightarrow & O. \\ & & | & & | & & \\ & & OH & & OH & & \end{array}$$

It is possible for more than two molecules of the ortho-acid to participate in this process of dehydration; polymeric metaphosphoric acids thus result (q.v.).

The simple B_2O_3 molecule, O=B—O—B=O, does not give rise to a tetrahydroxylated derivative $(HO)_2B—O—B(OH)_2$: further hydroxylation occurs at the oxygen link and $2B(OH)_3$ results. Tetraboric acid $2B_2O_3$, H_2O, may be a derivative of the polymerized oxide B_4O_6, thus:

$$\begin{array}{c} HO—B{=}O\rightarrow B—O—B\leftarrow O{=}B—OH, \\ \qquad\quad \| \qquad\; \| \\ \qquad\quad O \qquad\; O \end{array}$$

a formulation which might explain its ready decomposition in water to give meta- and ortho-boric acids, HBO_2 and H_3BO_3.

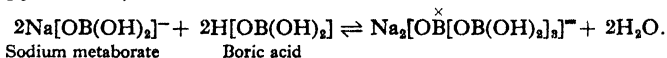
Physical investigations, e.g. conductivity, electrometric titrations, and cryoscopic measurements indicate the following equilibrium for H_3BO_3 in aqueous solution:

$$B(OH)_3 \rightleftharpoons H[OB(OH)_2] \rightleftharpoons BO_2' + H_3O.^+$$

Heat or titration with alkali produce BO_2^- ion, whilst in solvents of weaker dissociating power the equilibrium is displaced to the left yielding compounds of the type $B(OC_2H_5)_3$.

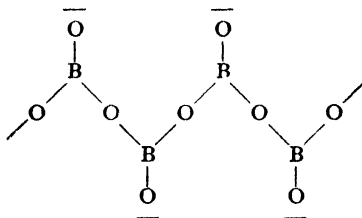
As a weak acid, boric acid condenses to form polyborates containing up to twelve boron atoms. These salts in dilute solution yield mainly BO_2^- ions and free boric acid.

This instability and rapidity of hydration of complex borate ions, coupled with the fact that boron can exhibit a maximum covalency of four, as in $[B(OC_2H_5)_4]Na$, leads to Hahn's

formulation (1931) of these polyborates. For the production of borax or sodium tetraborate (also named diborate or pyroborate) we have:

$$\underset{\text{Sodium metaborate}}{2Na[OB(OH)_2]^-} + \underset{\text{Boric acid}}{2H[OB(OH)_2]} \rightleftharpoons Na_2[O\overset{\times}{B}[OB(OH)_2]_3]^= + 2H_2O.$$

The boron atom marked × shows a co-ordination number of four.

It may be noted that X-ray analysis shows that the borate ion $(BO_3)^{\equiv}$ resembles the carbonate ion $(CO_3)^=$ in the co-planar triangular distribution of the oxygen atoms round the central atom: thus $InBO_3$ and $ScBO_3$ have the same structure as calcite, $CaCO_3$.

The study of solid calcium metaborate, $Ca(BO_2)_2$ has produced evidence showing that the triangular $(BO_3)^{\equiv}$ structure is evidently unstable and polymerizes by sharing oxygen atoms and giving a chain structure $(BO_2)_n^-$.

We have here the reason apart from solubility considerations why precipitated borates are generally the meta- and not the ortho-salts.

The gelatinous precipitate of so-called silicic acid, produced when acids act on alkali silicates, is an excellent example of the indefinite, unstable products which take the place of true hydroxides of the inner elements of the periodic table, particularly in the long periods. Such precipitates age on standing or heating, becoming less reactive. Their reactions tend to be colloidal, and in particular, amphoteric character can scarcely be distinguished from peptization of a colloid by

acid or alkali. In some cases, as with silica gel, the dehydration curve (vapour pressure against water content) gives no satisfactory evidence of hydrate formation, the substance behaving as a colloidal agglomerate of oxide and enmeshed water in varying proportions. Under controlled conditions of life-history, temperature, and water-vapour pressure, products can be produced which analyse to dubious hydrates, e.g. SiO_2H_2O. These indeterminate products are termed *hydrous* oxides to distinguish them from definite hydrates and hydroxides.

For the most part these hydrous oxides, e.g. those of SiO_2 and SnO_2, are amorphous to X-rays, but on drying develop the oxide pattern only.

The existence of a hydrous oxide does not preclude the possibility of hydroxide formation, for hydrous alumina may gradually form $Al(OH)_3$ and $AlO(OH)$, both of definite structure. Similarly, Wilstater (1928) considers that silicic acids from the mono- to the hexa-stage may exist in solution.

As a weak acid, silicic acid gives rise to salts of great complexity. These are discussed more fully later.

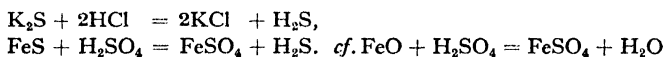
SULPHIDES

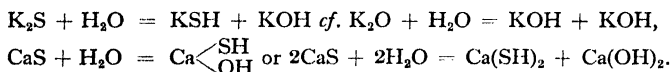
Sulphides possess the same general structure as oxides, and may be classified like them into basic, acidic, neutral, and persulphides, representatives of each class occupying corresponding positions in the periodic classification. A sulphide is a binary compound of sulphur with a less electro-negative element; hence the compounds of sulphur with the more electro-negative elements oxygen and chlorine are not sulphides of oxygen and chlorine respectively, but oxides and chlorides of sulphur. The less powerful electro-negative character of sulphur as compared with oxygen serves to account for the difference in properties between oxides and sulphides.

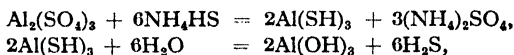
The affinity of a less electro-negative element for oxygen will naturally be superior to its affinity for sulphur, whence follows the very general reaction for the conversion of a

sulphide into an oxide by heating or exposure to air, as illustrated in the mode of extracting many metals from their native sulphides. The reaction is determined by the affinity both of the metal and of sulphur for oxygen, as well as by the volatility of sulphur dioxide; it may result in oxidation to sulphate, as in the roasting of lead sulphide, and in the conversion of precipitated copper sulphide into sulphate by exposure in the moist condition to air.

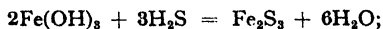
The character of a sulphide may be predicted from that of the corresponding oxide. A metallic sulphide, for instance, will yield salts and sulphuretted hydrogen by the action of acids, thus:

$$K_2S + 2HCl = 2KCl + H_2S,$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S. \quad cf.\ FeO + H_2SO_4 = FeSO_4 + H_2O$$

If the oxide is alkaline the sulphide will dissolve in water, forming a mixture of hydrosulphide and hydroxide.

$$K_2S + H_2O = KSH + KOH \quad cf.\ K_2O + H_2O = KOH + KOH,$$
$$CaS + H_2O = Ca\genfrac{<}{}{0pt}{}{SH}{OH} \text{ or } 2CaS + 2H_2O = Ca(SH)_2 + Ca(OH)_2.$$

If the oxide is feebly basic the sulphide will be decomposed by water, forming the hydroxide, with evolution of hydrogen sulphide. This is the case with aluminium and chromic sulphides of the type M_2S_3, which can neither be prepared nor exist in presence of water. Hence ammonium sulphide precipitates hydroxides from solutions of aluminium and chromic salts; thus:

$$Al_2(SO_4)_3 + 6NH_4HS = 2Al(SH)_3 + 3(NH_4)_2SO_4,$$
$$2Al(SH)_3 + 6H_2O = 2Al(OH)_3 + 6H_2S,$$

and similarly with chromium.

In the case of ferric iron the corresponding sulphide is formed by the action of hydrogen sulphide on the hydroxide, thus:

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O;$$

but this is gradually converted by excess of hydrogen sulphide into a mixture of di- and mono-sulphides, thus:

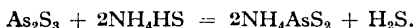
$$Fe_2S_3 = FeS_2 + FeS.^*$$

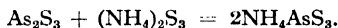
Many acidic oxides have, corresponding with them, sulphides less powerfully acidic than themselves. Thus CS_2 is the thio-anhydride of thio-carbonic acid H_2CS_3, and dissolves in sodium sulphide solution, forming sodium thio-carbonate.

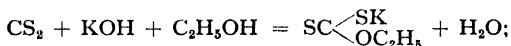
The following reactions are therefore analogous:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O,$$
$$2NaSH + CS_2 = Na_2CS_3 + H_2S.$$

Arsenious sulphide is likewise a thio-anhydride, and dissolves in ammonium sulphide, forming ammonium meta-thioarsenite:

$$As_2S_3 + 2NH_4HS = 2NH_4AsS_2 + H_2S.$$

If yellow ammonium polysulphide is used, a meta-thioarsenate is formed:

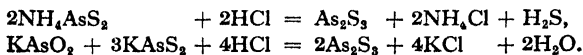
$$As_2S_3 + (NH_4)_2S_3 = 2NH_4AsS_3.$$

When a hydroxide is employed to dissolve a sulphide an oxythiosalt results; thus with potassium hydroxide and alcohol, carbon disulphide gives potassium xanthate,

$$CS_2 + KOH + C_2H_5OH = SC\begin{matrix}\diagup SK \\ \diagdown OC_2H_5\end{matrix} + H_2O;$$

and when arsenious sulphide dissolves in potash, a mixture of arsenite and thio-arsenite is produced; thus:

$$2As_2S_3 + 4KOH = KAsO_2 + 3KAsS_2 + 2H_2O.$$

Sulphides of antimony and tin behave similarly with alkalis.

By the addition of hydrochloric acid to solutions of these thio- or mixed thio- and oxy-salts, the reaction is reversed and the sulphide is reprecipitated; thus:

$$2NH_4AsS_2 + 2HCl = As_2S_3 + 2NH_4Cl + H_2S,$$
$$KAsO_2 + 3KAsS_2 + 4HCl = 2As_2S_3 + 4KCl + 2H_2O.$$

* V. Rodt, *Zeitsch. angew. Chem.* (1916), **29**, i, 422.

The less powerfully acidic properties of sulphides as compared with oxides are further shown by the easy decomposition of these thio-salts by acids. Few thio-acids indeed are known in the free state.

The formation of superoxides by linkage of oxygen atoms is paralleled among the sulphides by an analogous power of linkage of sulphur atoms. The chain-forming ability of sulphur is, however, superior to that of oxygen; persulphides of the type M_2S_n or MS_n, for instance, of the alkali and alkaline earth metals, are easily formed from the simple sulphides by direct combination with sulphur, and these so-called polysulphides—in reality supersulphides—often contain a larger proportion of sulphur than corresponds to oxygen in the superoxide.

When sulphur is boiled with a solution of sodium sulphide the compounds Na_2S_2 and Na_2S_4 are formed; similarly milk of lime takes up sulphur, forming CaS_2 and CaS_5, and from solutions of these substances H_2S_2 and H_2S_3 are produced by the action of acids.

There are no oxygen analogues of Na_2S_4, CaS_5, and H_2S_3. At the same time it may be mentioned that there is no oxygen analogue of the molecule of S_6, of which calcium pentasulphide may perhaps be a derivative.

The series of thionic acids, formulated on the general type $S_x(SO_2 \cdot OH)_2$ where $x = 1$ to 3, further illustrates the same tendency to form chains, exhibited by sulphur atoms. Similar oxygen acids, $O_x(SO_2 \cdot OH)_2$, where $x = 1$ or 2, are known. They are pyro- and persulphuric acid respectively.

HALIDES

Halides, or binary compounds of the elements fluorine, chlorine, bromine, and iodine with the other elements, are formed by nearly every element, and are, therefore, like oxides, excellently adapted to serve as a basis for comparison of chemical properties.

Direct union constitutes a general method of formation of

halides. Fluorine combines with every metal and most non-metals, at the ordinary temperature, and the readiness with which combination occurs between a halogen and another element decreases in passing from fluorine to iodine.

The halides of elements giving exclusively basic oxides, that is, halides corresponding with basic oxides, are salts, and are distinguished clearly from halides of electro-negative elements, that is, halides corresponding with acidic oxides. They are produced by the general methods for the preparation of metallic salts; that is, by the action of a metal, oxide or hydroxide, on a halogen acid, or by double decomposition. They are usually non-volatile solids, which are stable on heating, but are decomposed by strong sulphuric acid, with liberation of the volatile halogen acid. They are generally soluble in water, though insoluble in non-hydroxylic solvents such as ether, benzene, and chloroform. They undergo electrolytic dissociation in aqueous solution into ions of metal and halogen, and are recoverable unchanged from such solution on evaporation.

These rigorous criteria are true in the fullest sense for the halides of the alkali metals, MX, alone; but they also apply with limitations to the metallic halides, MX_2, especially to BaX_2.

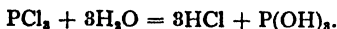
The properties of a halide of a typically non-metallic or electro-negative element are essentially different from the above. Halides of this class are usually obtained by direct union of the elements, or, in the case of chlorides, by passing chlorine over a heated mixture of an oxide of the element and carbon. This is a method particularly useful for obtaining chlorides of the less electro-negative of the non-metals, as, for example, silicon.

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

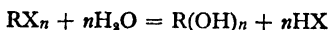
Typical non-metallic halides are stable when heated, but are easily volatile, often being liquids or solids of low melting-point. They are soluble in non-hydroxylic solvents, and are

unaffected by strong sulphuric acid; they have a pungent odour, and are decomposed by water, giving mixtures in solution of halogen acid and oxyacid corresponding with the oxide analogous to the halide.

These properties are well illustrated by the chlorides of phosphorus, which are readily acted on by water, heat being generated, and a solution of halogen acid and a corresponding acid of phosphorus being formed. Thus:

$$PCl_3 + 3H_2O = 3HCl + P(OH)_3.$$

Mendeléeff uses the term *chloranhydrides* for such chlorides as yield oxyacids on complete decomposition by water; a convenient general term inclusive of all such analogous halides would be *halanhydrides*. Thus PCl_3, $SiCl_4$, PBr_5, are halanhydrides; and the oxyacids formed by their decomposition by water are phosphorous, silicic, and phosphoric acids, halogen hydracid being produced at the same time.

Since the general reaction

$$RX_n + nH_2O = R(OH)_n + nHX$$

is here involved, the oxyacid formed might be expected to contain as many hydroxyl groups as the halanhydride contained halogen atoms, the latter being the ortho-halide of the acid. With the highest halides of phosphorus this is not so, the true ortho-acid, $P(OH)_5$, being unknown. Consequently, when phosphorus pentachloride reacts with water the following change takes place:

$$PCl_5 + 5H_2O = PO(OH)_3 + H_2O + 5HCl,$$

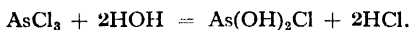
$POCl_3$ being formed as an intermediate product in the reaction. Sulphur hexafluoride SF_6 is a stable gas that is not hydrolysed by water.

The halides of phosphoric and sulphuric acids respectively are POX_3 and SO_2X_2; but these compounds are oxyhalides of the elements, and are better not described as halanhydrides, this term being reserved for the halides of true ortho-acids

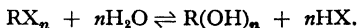
which at the same time are halides of non-metallic elements.

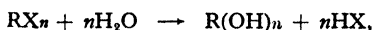
It appears from the consideration of PCl_5 and other non-metallic chlorides that full chlorination is more easily realizable than full hydroxylation. As before observed, inability to retain in stable union the maximum possible number of hydroxyl groups is a general characteristic of a non-metallic atom.

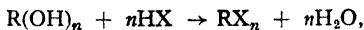
The halides of metals whose hydroxides are feeble bases—in some instances behaving as acids in relation to strong alkalis—are of an intermediate character, falling between the true metallic salt and the true halanhydride. They are distinguished often by being more volatile than the true metallic halides, but particularly by their ready decomposition by water, with production of oxy- or basic halides. Aluminium chloride is a good example of such a halide. It is an easily volatile solid which dissolves in water with evolution of heat and partial hydrolysis; on evaporation of the solution the oxide remains. Arsenious chloride is likewise an interesting example. It is a liquid, the first action of cold water upon which is as follows:

$$AsCl_3 + 2HOH = As(OH)_2Cl + 2HCl.$$

On warming with water the hydrolysis is completed, $As(OH)_3$ being formed. The compound $As(OH)_2Cl$ may be regarded either as a basic salt or a chloro-acid, from one or other point of view.

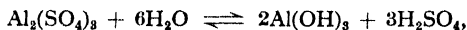
Not only are aluminium, arsenious, and similar halides decomposed by water, but they are generated from the hydroxides by excess of halogen acid; these two changes being represented by the reversible reaction,

$$RX_n + nH_2O \rightleftharpoons R(OH)_n + nHX.$$

This reversibility is on account of the intermediate character of such halides between halanhydrides and salts; the non-reversible reaction,

$$RX_n + nH_2O \longrightarrow R(OH)_n + nHX,$$

being characteristic of halanhydride decomposition, and the non-reversible reaction,

$$R(OH)_n + nHX \rightarrow RX_n + nH_2O,$$

of salt-formation.

Comparable with the halides are the oxysalts. For instance, aluminium sulphate undergoes hydrolysis according to the following reaction:

$$Al_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Al(OH)_3 + 3H_2SO_4,$$

a basic salt being in fact produced; but potassium sulphate, a true salt, is not hydrolyzed by water.

Many halides, in particular fluorides and chlorides of non-metals and weak metals, display the property of readily yielding double or complex salts with metallic halides, and more or less stable acids by union with halogen acids in solution. Such are $PtCl_2$ giving K_2PtCl_4, $PtCl_4$ giving K_2PtCl_6, and H_2PtCl_6, $6H_2O$, $AuCl_3$ giving $KAuCl_4$, $AuBr_3$ giving $KAuBr_4$, the fluorides of silicon, germanium, and tin giving K_2XF_6, and BF_3 giving KBF_4. This property is comparable with that of the formation of double or complex cyanides by many metallic cyanides, especially those of the eighth group (q.v.).

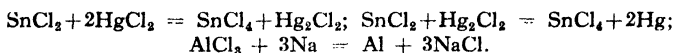
It may be suggested that the union of basic and acidic halides to form complex salts is analogous on the one hand to combination between basic and acidic oxides to form simple salts, and on the other hand to union between sulphates such as those of potassium and aluminium with the formation of alums and other double salts.

CHAPTER IV

OXIDATION AND REDUCTION

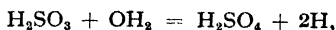
The processes of oxidation and reduction are amongst the most widely occurring general reactions of chemistry. They are consequently valuable for comparative purposes; and because of the light they throw on the mechanism of many reactions, otherwise obscure, it is desirable to classify these processes, and to study the conditions of their action.

As a first approximation the following definitions may be given: Oxidation consists in the combination of oxygen with an elementary or compound substance. Reduction is the converse process, or the withdrawal of oxygen from a substance containing it. Limitations and extensions of this simple idea at once suggest themselves. For example, can the loss of oxygen by the application of heat, and decomposition by the agency of the electric current, be classed as examples of this process? It is evident that the addition or abstraction of oxygen is not the sole characteristic of these reactions. Some other element, notably chlorine, or a complex acidic radicle, may be the component added or withdrawn, as in cases of reduction of metallic chlorides either to lower chlorides or to metals, for example, in the reactions:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2; \quad SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg;$$
$$AlCl_3 + 3Na = Al + 3NaCl.$$

The chlorination of a metal or chloride is generally possible by the direct action of chlorine alone, as in the production of $SnCl_4$ from $SnCl_2$ and $HgCl_2$ from Hg_2Cl_2, the element added itself performing a function analogous to oxidation; just as oxygen may oxidize a metal to an oxide, or a lower to a higher oxide.

In some cases, abstraction or addition of hydrogen may constitute oxidation or reduction respectively. Reduction of an

organic dye substance by sulphurous acid is due to this cause, as is shown by the following reaction:

$$H_2SO_3 + OH_2 = H_2SO_4 + 2H,$$

hydrogen being added on to the colouring matter with production of a leuco-compound.

A well-known instance of this mode of action with organic compounds is furnished by the interconversion of ketones and secondary alcohols.*

$$R_2 : CO \overset{2H}{\rightleftharpoons} R_2 : CH \cdot OH.$$

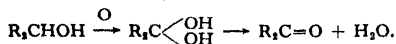
In the case of the complex cyanides, for instance potassium ferro- and ferricyanide, the electro-negative radicle (CN)′ may behave similarly to Cl in respect to oxidation and reduction processes. Passage from ferrocyanide, $K_4Fe(CN)_6$, to ferricyanide, $K_3Fe(CN)_6$, involves essentially a change from $Fe(CN)_2$ to $Fe(CN)_3$, parallel to the conversion of $FeCl_2$ into $FeCl_3$, or FeO into Fe_2O_3, and is therefore to be classed as an oxidation process.

Oxidation may therefore be described as the *conversion of a compound representing a lower into one representing a higher stage of combination with oxygen, by the addition either of oxygen, or an equivalent electro-negative atom or radicle, or by the removal of hydrogen or an electro-positive atom or radicle.*

Reduction may be defined as the result of the converse operations.

Among inorganic compounds, oxidation usually denotes an increase in the active valency of the central atom, as in examples already given. Increase of valency is not, however a necessary concomitant of oxidation; for no such increase takes place in the conversion of an oxide into a superoxide, for instance, BaO into BaO_2, or H_2O into H_2O_2.

* Organic oxidation processes, resulting in the abstraction of hydrogen, are, however, best considered as proceeding through the intermediate addition of oxygen. This is the case in the oxidation of secondary alcohols, as is shown by the scheme

$$R_2CHOH \xrightarrow{O} R_2C\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix} \longrightarrow R_2C{=}O + H_2O.$$

Oxidizing and Reducing Agents.—To effect the changes discussed above, certain chemical substances are employed as oxidizing or reducing agents. An *oxidizing agent* may be defined, in most general terms, as *a substance, elementary or compound, capable of increasing the proportional content in electro-negative atoms or groups of the molecule of a given substance, either by actual increase in the number of such atoms or groups within the molecule, or by the removal of a more electro-positive component.*

The converse proposition defines a *reducing agent* as *a substance capable of decreasing the proportion of electro-negative atoms or groups within the molecule of an element or compound.*

An oxidizing agent is therefore an element or compound possessing affinity for, and easily combining with, an electro-positive element or group.

A reducing agent is similarly a substance possessing affinity for an electro-negative atom or group.

In the operation of a reagent of either kind, reduction is suffered by the oxidizing agent, and oxidation by the reducing agent. The most powerful oxidizers are therefore characterized by ready reducibility, and the most powerful reducers by ready oxidizability.

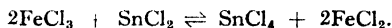
Among the *common oxidizing agents* may be enumerated *oxygen, ozone, peroxides, oxyacids such as nitric acid, the halogens with their oxyacids and their salts*, and acids corresponding with higher metallic oxides, such as *chromic and permanganic acids and their salts*; also certain *unstable basic oxides*, such as those of *silver and gold*. All these substances operate directly. Chlorine operates either by the liberation of oxygen from hypochlorous acid ($2Cl + H_2O = HCl + HOCl$), by direct chlorination, or by the abstraction of hydrogen or a metal.

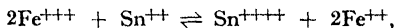
Common reducing agents are: *hydrogen, gaseous and so-called nascent, unstable hydrides*, such as *hydriodic acid and the hydrides of sulphur, selenium, tellurium, phosphorus, arsenic, antimony, and silicon; carbon;* many metals, such as *sodium, potassium, magnesium*, which act by virtue of their affinity for oxygen or

other electro-negative elements; lower oxides, such as *carbon monoxide*, and lower oxyacids and salts, such as *hypophosphites*, *phosphites*, and *sulphites*; salts, such as *potassium cyanide* and *formate*, which combine directly with oxygen under certain circumstances; and lower salts, such as *ferrous*, *chromous*, and *stannous salts*.

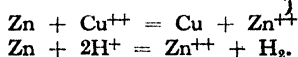
OXIDATION—REDUCTION MECHANISM

A more fundamental conception of oxidation and reduction reactions is obtained by a study of those occurring between ions in solution. Ferric chloride and stannous chloride in aqueous solution react thus:

$$2FeCl_3 + SnCl_2 \rightleftharpoons SnCl_4 + 2FeCl_2.$$

In terms of the ions solely concerned, this may be written:

$$2Fe^{+++} + Sn^{++} \rightleftharpoons Sn^{++++} + 2Fe^{++},$$

and it becomes evident that stannous ion is oxidized by the loss of two electrons which have passed to the ferric ions, reducing them to the ferrous state. In this we have the explanation of the valency changes undergone by such a system, and, furthermore, we plainly see that here, as in many similar examples, we are dealing, not with oxygen or hydrogen, but purely with electron interchange.

Hence, in such ionic systems, *oxidation* may be defined as a *loss of electrons*, and *reduction* as a *gain of electrons*; whence it follows that an *oxidizing agent readily removes electrons, whilst a reducing agent readily furnishes electrons*, to effect these processes. Such a definition of oxidation brings other reactions within its scope, for, when zinc displaces copper from aqueous copper sulphate, or liberates hydrogen from an acid, it is oxidized to Zn^{++} by the loss of two electrons, while the ions, Cu^{++} or H^{+}, acquire these electrons and appear as the neutral atom or molecule, thus:

$$Zn + Cu^{++} = Cu + Zn^{++}$$
$$Zn + 2H^{+} = Zn^{++} + H_2.$$

Electrolytic processes are also included.

That electron transfer, and not simply molecular contact, is the basis of these reactions can be demonstrated by separating the reactants in a suitable oxidation-reduction cell. For details suitable textbooks must be consulted.

We have seen already that a metal in contact with a molar solution of its ions acquires its Normal Electrode Potential. In similar fashion, if an unattackable electrode, e.g. a platinum wire, be introduced into a solution containing ions of any one element, some in the oxidized, and some in the reduced state, and in equilibrium, thus, $M^+ \rightleftharpoons M^{++} + E$, the electrode will acquire a positive or negative potential according as the system tends to be oxidizing (i.e. to remove electrons) or reducing (i.e. to give up electrons). Consequently, this electrode potential will be a measure of the oxidizing or reducing tendency of the solution. For a solution containing both ions in equal amounts, the value will be the Normal (or Standard) Oxidation-Reduction Potential of the particular system.

The *intensity*, or driving power, of such a system is not constant, but depends on the ratio of the two ions present, being greater when the oxidized ion is in excess. It also varies with temperature, and, in many cases, with the concentration of hydrogen ions.

The formation of complex ions, or of insoluble products will affect the intensity. Thus, a solution of ferric and ferrous ions in equal amount slowly reduces $AgNO_3$; addition of KF solution removes the ferric ions as $[FeF_6]^{\equiv}$, when reduction by the ferrous ions proceeds immediately. The capacity of a system to oxidize (or reduce) some substance completely, depends on its molecular concentration; there must be sufficient present to complete the oxidation (or reduction). The table of Normal Oxidation-Reduction Potentials below shows their relative nature.

The values given are valid only for the conditions under which they were measured, and are applicable theoretically only when the reaction concerned is reversible in the thermo-

dynamical sense. The existence of potentials for complexer systems means that, in spite of our ignorance of the reactions involved, we are justified in treating them simply as electron exchanges. Some values, however, are merely comparative.

$Co^{+++} \rightleftharpoons Co^{++}$ (acid)		+1·8 volts.
$MnO_4^- \rightleftharpoons Mn^{++}$ (N. acid)		1·52
$Ce^{++++} \rightleftharpoons Ce^{+++}$ (HNO_3)		1·5
$Cl_2 \rightleftharpoons 2Cl^-$		1·36
$Cr_2O_7^= \rightleftharpoons Cr^{+++}$ (acid)		1·3
$Fe^{+++} \rightleftharpoons Fe^{++}$		0·75
$I_2 \rightleftharpoons 2I^-$		0·53
$MnO_4^- \rightleftharpoons MnO_2$ (N. alkali)		0·52
$Cu^{++} \rightleftharpoons Cu^+$		0·20
$Ti^{++++} \rightleftharpoons Ti^{+++}$ (H_2SO_4)		0·04
$H_2 \rightleftharpoons 2H^+$		0·00
$Cr^{+++} \rightleftharpoons Cr^{++}$		−0·41
$Sn^{++++} \rightleftharpoons Sn^{++}$		−0·40

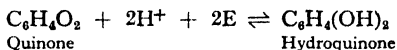
The greater the potential, the more readily will the oxidized form gain electrons and become reduced, hence, any system will be oxidizing to those below it, but itself will be oxidized by those above it.

When, therefore, the oxidized ion $(MnO_4)'$ of permanganate is added to Fe^{++} ion (the reduced form) in presence of acid, the superior potential of the permanganate system will cause it to reduce while it oxidizes the ferrous to ferric ion.

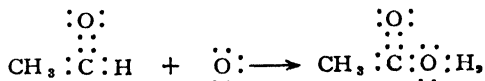
When an oxidation-reduction system is influenced by acidity it will be found that acid increases its potential, while alkali lowers it. It often happens that when an oxidant and reductant are present in the same alkaline medium, the potential of the reductant is diminished to a greater extent. It thus becomes a more powerful reducing agent and is more readily oxidized. This is the more precise statement of the qualitative fact that lower basic oxides and their derivatives will oxidize more readily if alkali be present, the oxidized products being less liable to reduce again. In spite of its inferior oxidizing intensity, alkaline $KMnO_4$ is extensively used to oxidize organic compounds, partly because some products are acidic in

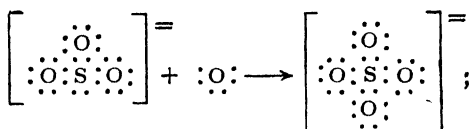
character, and because in some cases the reducing property of the organic substance is enhanced by alkali.

Several organic oxidation-reduction systems are known to be reversible, as with methylene blue, and the quinone-hydroquinone change utilized to determine hydrogen ion concentration.

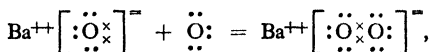
$$\underset{\text{Quinone}}{C_6H_4O_2} + 2H^+ + 2E \rightleftharpoons \underset{\text{Hydroquinone}}{C_6H_4(OH)_2}$$

We may inquire, however, if this fundamental idea of electron interchange can be extended to compounds where the linkage is covalent, or to compounds where no valency change occurs. The answer is, that such oxidations are better defined in terms of oxygen and hydrogen.

We do not consider that electron transfer occurs when acetaldehyde is oxidized to acetic acid, thus:

$$CH_3:\overset{:O:}{\underset{}{\overset{\cdot\cdot}{\underset{}{\overset{\cdot\cdot}{C}}}}}:H \quad + \quad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \longrightarrow CH_3:\overset{:O:}{\overset{\cdot\cdot}{\underset{}{\overset{\cdot\cdot}{C}}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H,$$

nor when sulphite forms sulphate thus:

$$\left[\begin{matrix} & :\overset{\cdot\cdot}{O}: & \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{S}} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \end{matrix}\right]^{=} + \ :\underset{\cdot\cdot}{O}: \longrightarrow \left[\begin{matrix} & :\overset{\cdot\cdot}{O}: & \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{S}} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \\ & :\underset{\cdot\cdot}{O}: & \end{matrix}\right]^{=};$$

although the sulphur atom is conventionally regarded as passing from the quadri- to the sexi-valent state.

The oxidation of BaO to form BaO_2 involves no valency change in the Ba atom. Barium oxide is ionic, and the change may be shown electronically, thus:

$$Ba^{++}\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\substack{\times\\ \times}\right]^{=} + \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: = Ba^{++}\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\substack{\times\\ \times}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\right]^{=},$$

We might infer that by sharing two electrons (×), one oxygen atom has been oxidized, while the acceptor atom has been reduced. But in a similar case, when the cupric ion Cu^{++}

forms $[Cu(NH_3)_4]^{++}$ by co-ordination, we do not say that copper has been reduced.

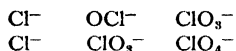
The mutual oxidation and reduction of hypochlorite ions to chlorate and chloride may be represented thus:

$$\left[:\ddot{\underset{\cdot\cdot}{O}}\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{Cl}}:\right]^- + 2\left[:\ddot{\underset{\cdot\cdot}{O}}\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{Cl}}:\right]^- = \left[:\ddot{\underset{\cdot\cdot}{O}}\overset{\times}{\cdot}\ddot{\underset{\underset{O}{\cdot\cdot}}{Cl}}:\ddot{\underset{\cdot\cdot}{O}}:\right]^- + 2\left[\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{Cl}}:\right]^-.$$

On Grimm and Sommerfeld's criterion of valency, each chlorine atom initially has a valency of +1, since one only (×) of its seven electrons is used in the covalent link with oxygen. In the chlorate ion, the valency of chlorine is +5, five of its electrons being used to link oxygen. The two remaining chlorine atoms, originally of valency +1, are now reduced to chloride ions of valency −1. The chlorate ion may suffer further oxidation to perchlorate $[ClO_4]^-$, in which all seven electrons are utilized, and the valency of chlorine is +7.

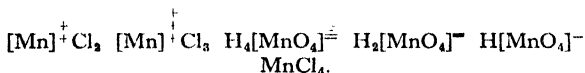
The charge on the ions is constant, and throughout the oxidation and valency changes, the contribution of seven electrons made by chlorine to its valency group is unchanged. Progressive oxidation occurs as each unused electron pair is utilized to bond oxygen atoms.

In the series of progressively oxidized ions;

$$\begin{array}{ccc} Cl^- & OCl^- & ClO_3^- \\ Cl^- & ClO_3^- & ClO_4^- \end{array}$$

it should be noted that the hypochlorite ion is a stronger oxidizing agent than chlorate ion, the latter being more strongly oxidizing than perchlorate ion. It is true generally that, when an ion undergoes self-oxidation and reduction, that ion is a stronger oxidizing agent than the resultant oxidized ion.

The manganese analogue of $KClO_4$ is $KMnO_4$, and, as befits the transitional character of manganese, it undergoes smooth and quantitative changes. Indeed its versatility forms an interesting study of oxidation and reduction from the electronic point of view, and may be contrasted with chlorine.

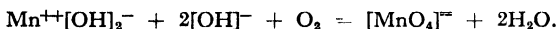
Consider the following manganese compounds:

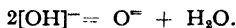
$$[Mn]^{++}Cl_2 \quad [Mn]^{+++}Cl_3 \quad H_4[MnO_4]^{----} \quad H_2[MnO_4]^{--} \quad H[MnO_4]^{-}$$
$$MnCl_4.$$

Ions are contained in square brackets, and their valencies are represented by + or — signs, indicating basic or acidic ions.

Further, + signs indicate electrons cast off frcm the valency group of manganese, and so contributing to the making of acidic ions by other elements; and — signs indicate electrons gained by the valency groups from an outside source, and then employed to bind oxygen and form acidic radicles. Thus manganese forms two basic ions containing the metal alone, and three acidic ions in which the metal is associated with oxygen, while $MnCl_4$ is a covalent molecule.

Now manganese has the atomic number 25, i.e. 25 electrons are external to the nucleus of the central atom, and having the quantum arrangement shown later. Only when the bivalent ion, Mn^{++}, is formed are the two electrons of the last quantum group sufficient: in other cases electrons must be imported for valency purposes. These may come either from the third quantum group of the manganese atom itself, or, as shown by the charge on the oxy-ions, come from an external source.

The electronic changes accompanying the formation of such an oxy-ion may be elucidated by considering the action of fused alkali on $Mn(OH)_2$ in presence of air. The reaction is essentially:

$$Mn^{++}[OH]_2^{-} + 2[OH]^{-} + O_2 = [MnO_4]^{=} + 2H_2O.$$

Each pair of hydroxyl ions reacts thus:

$$2[OH]^{-} = O^{=} + H_2O.$$

Hence the Mn atom retains one oxygen atom and two bonding electrons, at the same time it acquires the oxygen ion, $O^{=}$, liberated by decomposition of the alkali hydroxyl ions, whereby the negative charge on the oxy-ion arises. To co-ordinate two neutral oxygen atoms from the air, the manganese atom withdraws four more electrons from its inner group. The ion

$[MnO_4]^{-}$, therefore, requires manganese to contribute in all six electrons, the remaining two coming from an external source.

The structure of the manganese atom in its ions may be thus represented:

[Mn]	2	2	2	4	2	2	4	5	2
$[Mn]^{++}$	2	2	2	4	2	2	4	5	(2) ↗
$[Mn]^{+++}$	2	2	2	4	2	2	4	4	(3) ↗
$[MnO_4]^{----}$	2	2	2	4	2	2	4	3	4 (4) ↙
$[MnO_4]^{--}$	2	2	2	4	2	2	4	1	6 (2) ↙
$[MnO_4]^{-}$	2	2	2	4	2	2	4		7 (1) ↙

The figures in brackets represent electrons either to be lost (↗), i.e. to be contributed, say to halogen atoms to convert them into ions, or to be gained (↙) from hydrogen or metallic atoms, which accordingly become ions.

The oxy-ions, including the hypothetical orthomanganite ion, all differ in the number of electrons to be provided by the manganese atom, and therefore in the number of negative charges to be brought from outside. The valency of manganese, as distinct from that of its ions, is reckoned by the number of electrons which it itself provides for ion formation. On modern theories, however, the Mn atom in $[MnO_4]^{-}$, as with Cl in $[ClO_4]^{-}$ may be described as 4-covalent.

In the compound, $MnCl_4$, manganese has provided four electrons for its valency group, which it employs to bind the four chlorine atoms to itself by covalency. It is possible, however, for manganese to accommodate six Cl atoms in its periphery, for the complex salt K_2MnCl_6 exists. This arises because the Cl ions of 2KCl, each with eight electrons, may co-ordinate with the Mn atom, each by a pair of its own electrons, to form the ion $[MnCl_6]^{=}$, thus introducing the double charge.

The resting stage for the reduction of permanganate in alkaline solution is the hypothetical ion $[MnO_4]^{\equiv}$, as evidenced by the production of MnO_2. Alkali has so reduced the oxidizing potential of this stage that no further reduction is evident. In acid solution, however, this inhibition does not occur; indeed the potential is raised, and the reduction proceeds to Mn^{++}.

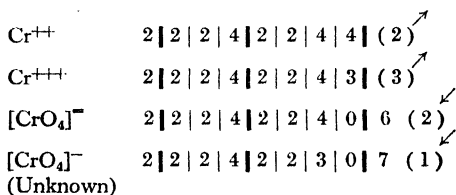
Since ions only are concerned in these reactions, the equations representing them should be ionic. Thus when permanganate is reduced to manganous salt, manganese is reduced from septi- to bi-valency by the addition of 5E, which may be derived from $5Fe^{++}$ thus:

$$MnO_4^- + 5E = Mn^{++} + 4O^{--}$$
$$5Fe^{++} - 5E = 5Fe^{+++}$$
$$\text{and} \quad 4O^{--} + 8H^+ = 4H_2O$$

$$\text{Adding: } MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O.$$

The final equation represents essentially the oxidation of ferrous iron in acid solution by permanganate.

The following ions of chromium (At. No. 24) are parallel to those of manganese.

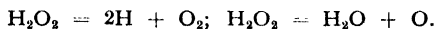
Cr^{++}	2 ǀ 2 | 2 | 4 ǀ 2 | 2 | 4 | 4 ǀ (2)
Cr^{+++}	2 ǀ 2 | 2 | 4 ǀ 2 | 2 | 4 | 3 ǀ (3)
$[CrO_4]^=$	2 ǀ 2 | 2 | 4 ǀ 2 | 2 | 4 | 0 ǀ 6 (2)
$[CrO_4]^-$ (Unknown)	2 ǀ 2 | 2 | 4 ǀ 2 | 2 | 3 | 0 ǀ 7 (1)

The third quantum group in $[CrO_4]^=$ contains 8 electrons, and is too stable to part with a further electron to form a "perchromate" analogous to permanganate. Again, the ion, Cr^{+++}, is the usual reduction state, the change, $Cr^{+++} \rightleftharpoons Cr^{++}$ requiring vigorous reducing agents, and being easily reversible.

Alkaline $[CrO_4]^=$, unlike $[MnO_4]^=$, is stable and shows no oxidizing properties.

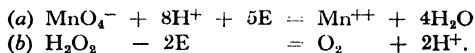
Hydrogen peroxide in alkaline solution oxidizes chromic salt to chromate; in acid solution the reverse change occurs.

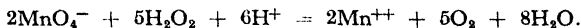
This dual rôle of oxidant and reductant is difficult to interpret. According to Bancroft (1935), hydrogen peroxide in acid solutions of molar strength has an oxidizing potential of approximately +1·16 volts; in molar alkali the value is +0·03 volt. Consequently, if the potential for any oxidizing or reducing agent is greater than the appropriate potential of hydrogen peroxide in the same acid or alkaline solution, that substance will be reduced. If the potential is smaller, it is oxidized.

The source of the oxygen liberated when H_2O_2 acts as a reducing agent has been a matter of controversy. Traube and Baeyer believed that it all came from the hydrogen peroxide; according to Schönbein and Berthelot, only one-half is so derived.

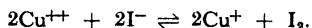
$$H_2O_2 = 2H + O_2; \quad H_2O_2 = H_2O + O.$$

The first is most probable, and is supported by Wieland's work on the catalytic decomposition of H_2O_2, which is shown to be initially a dehydrogenation.

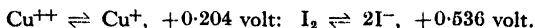
In acid solution, $KMnO_4$ and H_2O_2 are oxidizing and reducing agents, respectively.

$$(a)\ MnO_4^- + 8H^+ + 5E = Mn^{++} + 4H_2O$$
$$(b)\ H_2O_2 - 2E = O_2 + 2H^+.$$

Multiplying (*a*) by 2 and (*b*) by 5, we get, on adding,

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 5O_2 + 8H_2O.$$

It will be noted that increased concentration of H^+ favours reaction (*a*) but tends to retard reaction (*b*), though this effect is small since gaseous oxygen leaves the system.

The production of cuprous rather than cupric iodide when KI is added to a cupric salt solution is essentially:

$$2Cu^{++} + 2I^- \rightleftharpoons 2Cu^+ + I_2.$$

The potentials of the reactions concerned are:

$$Cu^{++} \rightleftharpoons Cu^+, +0{\cdot}204 \text{ volt: } I_2 \rightleftharpoons 2I^-, +0{\cdot}536 \text{ volt.}$$

Calculations based on these values, and on typical ionic concentrations show that the very small amount of Cu^+ ion

present at equilibrium is removed as the very insoluble iodide, thus enabling the reaction to proceed. The higher potential (+1·36) for $Cl_2 \rightleftharpoons 2Cl^-$, and greater solubility of cuprous chloride, ensures the stability of cupric chloride.

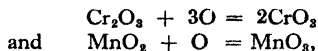
The reactions below further illustrate these principles, though some are discussed from different viewpoints.

MODES OF APPLICATION

Oxidation in the Dry Way

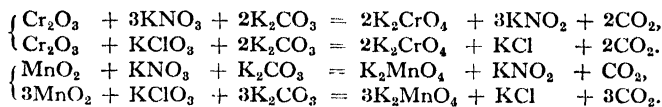
Oxidation may be effected in the dry way with the aid of heat. The production of oxides, and of some higher oxides from lower oxides, by direct union, illustrates this method. Examples are the production of an oxide by heating an element such as sulphur, phosphorus, sodium, magnesium, zinc, mercury, lead, or iron in air or oxygen, and the formation of certain higher oxides, such as red-lead, Pb_3O_4, and barium peroxide, BaO_2, by heating the lower oxides, PbO and BaO, in air.

Oxidation by fusion, or powerful heating with highly oxygenated salts, belongs to the same category; for instance, the action of potassium chlorate or nitrate on sulphur, sulphides, and carbon. The production of acidic from basic oxides by this process is of importance analytically and technically. Such acidic oxides are often unstable when heated in the free state, and therefore are not formed by the direct union of basic oxides with oxygen. The presence of caustic alkali or carbonate renders the oxidation by chlorate, nitrate, or atmospheric air at high temperature permanent by the formation of a stable salt of the higher oxide. This process is best illustrated by the oxidation of chromic oxide and manganese dioxide by fusion with alkali, together with an oxidizing agent, or with free exposure to air. The reactions are essentially

$$Cr_2O_3 + 3O = 2CrO_3$$
and
$$MnO_2 + O = MnO_3,$$

chromate and manganate, e.g. K_2CrO_4 and K_2MnO_4, being

produced in the actual operation. The nitrate or chlorate employed itself undergoes reduction to nitrite or chloride, so that the following equations represent the complete reactions:

$$\left\{\begin{array}{l} Cr_2O_3 + 3KNO_3 + 2K_2CO_3 = 2K_2CrO_4 + 3KNO_2 + 2CO_2, \\ Cr_2O_3 + KClO_3 + 2K_2CO_3 = 2K_2CrO_4 + KCl + 2CO_2. \end{array}\right.$$

$$\left\{\begin{array}{l} MnO_2 + KNO_3 + K_2CO_3 = K_2MnO_4 + KNO_2 + CO_2, \\ 3MnO_2 + KClO_3 + 3K_2CO_3 = 3K_2MnO_4 + KCl + 3CO_2. \end{array}\right.$$

Certain peroxides, such as those of lead and sodium, are useful as oxidizing agents in the dry way. Organic substances containing sulphur and phosphorus are oxidized when heated with excess of sodium peroxide, with formation of sodium sulphate, and phosphate.

Dry ozone oxidizes mercury and silver superficially at atmospheric temperature.

Oxidation in the Wet Way

Some substances are oxidized by atmospheric oxygen at ordinary temperature in presence of moisture. When phosphorus or iron borings are placed in contact with air and water in an enclosed space they gradually absorb the oxygen. The rusting of iron appears to be accelerated by the presence of carbon dioxide, and the corroding of lead consists in the formation of hydroxide in solution; thus, $2Pb + 2H_2O + O_2 = 2Pb(OH)_2$, and its precipitation as basic carbonate by the carbon dioxide present.

Ozone oxidizes certain substances in solution; for instance, it liberates iodine from potassium iodide,

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2;$$

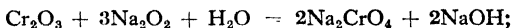
it also bleaches various colouring matters by oxidation, but reduces hydrogen peroxide thus:

$$O_3 + H_2O_2 = H_2O + 2O_2.$$

Hydrogen peroxide likewise behaves both as an oxidizing and as a reducing agent; its oxidizing action is generally manifested in neutral or alkaline solution, for instance, lead

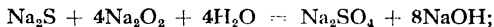
sulphide suspended in water is oxidized to sulphate and manganous hydroxide to the dioxide; whilst in acid solution reduction generally takes place, for example, permanganate and MnO_2 are reduced to manganous salt.

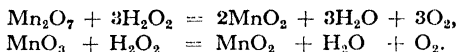
Sodium peroxide oxidizes chromic oxide in presence of water, producing chromate,

$$Cr_2O_3 + 3Na_2O_2 + H_2O = 2Na_2CrO_4 + 2NaOH;$$

lead peroxide behaves in a similar way in presence of alkali,

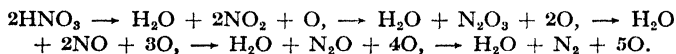
$$Cr_2O_3 + 3PbO_2 + 4KOH = 2K_2CrO_4 + 3PbO + 2H_2O.$$

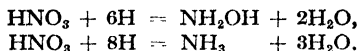
Sodium peroxide also oxidizes alkali sulphides to sulphates in solution,

$$Na_2S + 4Na_2O_2 + 4H_2O = Na_2SO_4 + 8NaOH;$$

and manganous compounds to hydrated manganese dioxide. Manganese compounds are not raised to a higher stage of oxidation than this by sodium peroxide in solution, since hydrogen peroxide is generated, which, under these circumstances, would reduce permanganates and manganates to manganese dioxide; thus:

$$Mn_2O_7 + 3H_2O_2 = 2MnO_2 + 3H_2O + 3O_2,$$
$$MnO_3 + H_2O_2 = MnO_2 + H_2O + O_2.$$

Oxyacids owe their oxidizing powers to the ease with which they part with oxygen.

Nitric acid suffers reduction in the following stages:

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O, \rightarrow H_2O + N_2O_3 + 2O, \rightarrow H_2O + 2NO + 3O, \rightarrow H_2O + N_2O + 4O, \rightarrow H_2O + N_2 + 5O.$$

Hydroxylamine and ammonia may likewise be produced; thus:

$$HNO_3 + 6H = NH_2OH + 2H_2O,$$
$$HNO_3 + 8H = NH_3 + 3H_2O.$$

Nitric acid may be used in a diluted or concentrated condition to oxidize metals or non-metals, oxides, sulphides, salts, and organic matter.

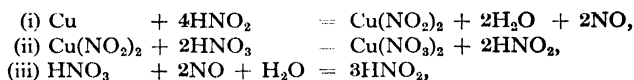
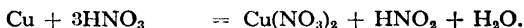
The nature of the reduction product depends upon the

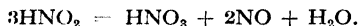
relative concentrations of acid and reducing agent, as well as upon the nature of the latter.

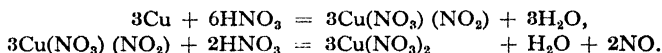
The mechanism of reduction of nitric acid by metals may here be discussed. Two views at first sight appear possible: either that nascent hydrogen is liberated from the acid by the metal, which in turn reduces more of the acid, or that the metal itself reduces the acid directly. Now the metals silver, mercury, copper, and bismuth have no perceptible action on cold, dilute sulphuric or hydrochloric acids; it is therefore unlikely that they will reduce nitric acid by the generation and agency of nascent hydrogen. As a matter of fact no gas is evolved when cold dilute nitric acid is used. If, however, the acid contains a trace of nitrous acid, or a lower oxide of nitrogen, or is warmed so as to induce incipient decomposition, action at once commences with evolution of nitric oxide and formation of metallic nitrate. The following reactions probably take place with copper, and similarly with the rest of these metals: *

$$\text{(i) } Cu + 4HNO_2 = Cu(NO_2)_2 + 2H_2O + 2NO,$$
$$\text{(ii) } Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2,$$
$$\text{(iii) } HNO_3 + 2NO + H_2O = 3HNO_2,$$

or adding

$$Cu + 3HNO_3 = Cu(NO_3)_2 + HNO_2 + H_2O.$$

The nitrous acid so produced then decomposes thus:

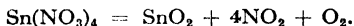
$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

An alternative view is expressed by the following equations: †

$$3Cu + 6HNO_3 = 3Cu(NO_3)(NO_2) + 3H_2O,$$
$$3Cu(NO_3)(NO_2) + 2HNO_3 = 3Cu(NO_3)_2 + H_2O + 2NO.$$

Those more electro-positive metals, which displace hydrogen perceptibly from dilute sulphuric acid and concentrated or dilute hydrochloric acids, may be supposed capable of reducing nitric acid through the agency of nascent hydrogen. They

* Veley, *Roy. Soc. Trans.* (1891), 182, A. 279–317.
† Stansbie, *J. Soc. Chem. Ind.* (1913), **32**, 311.

are magnesium, zinc, cadmium, iron, aluminium, tin, and lead. Whilst the former metals, silver, mercury, copper, and bismuth never reduce nitric acid to hydroxylamine or ammonia, those latter may produce these substances besides nitrous oxide and nitrogen (probably resulting from the interaction of nitrous acid and ammonia). Hydrogen itself, indeed, is among the gases evolved from dilute nitric acid by magnesium. It would be difficult to say how far nascent hydrogen and how far the metal itself is responsible for the reduction to nitrous acid and lower compounds; in the formation of ammonia nascent hydrogen must, however, play a part. Dilute nitric acid is reduced to ammonia by the zinc-copper couple, and also by iron filings in the presence of a little sulphuric acid.

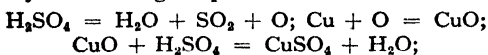
Nitrogen peroxide appears as a reduction product of nitric acid in certain cases, notably in the oxidation of red phosphorus, arsenious oxide, and organic compounds. It is also produced when moderately strong nitric acid reacts with metallic tin. In this case, however, it is not entirely a reduction product of nitric acid, for the stannic nitrate first produced is unstable, and breaks up thus:

$$Sn(NO_3)_4 = SnO_2 + 4NO_2 + O_2.$$

Thus when the metal has feebly electro-positive properties its most stable oxide is produced instead of the nitrate. Similarly antimony is oxidized to Sb_2O_5, and, passing to non-metals, phosphoric acid corresponding with P_2O_5, arsenic acid corresponding with As_2O_5, and iodic acid corresponding with I_2O_5 are produced. Sulphur is converted into sulphuric acid, but bromine and chlorine are not acted on by nitric acid.

Sulphuric acid also may act as an oxidizing agent. Metals which do not decompose steam on moderate heating, nor give hydrogen with dilute acids, as well as many that do both, are oxidized by hot strong sulphuric acid. Thus with copper:

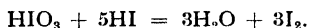
$$H_2SO_4 = H_2O + SO_2 + O; \; Cu + O = CuO;$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O;$$

or

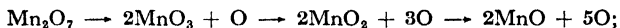
$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

Some of the sulphuric acid is generally reduced further by the excess of metallic copper with formation of Cu_2S, thus:

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O.$$

With carbon, sulphur dioxide and carbon dioxide are produced. Chloric, bromic, and iodic, as well as perchloric and periodic acids, and the oxides of chlorine and iodine, are oxidizing agents, the available oxygen being represented by the state of oxidation in which the halogen exists in these compounds above the condition of halide. Thus, for instance, iodic and hydriodic acids react upon one another as follows:

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

Oxidation by aqueous solutions of hypochlorites, hypobromites, and hypoiodites results from the ready decomposition of these salts, $NaOX = NaX + O$; a very good example is the oxidation of ammonia and amides such as urea to nitrogen; thus these compounds constitute a source of available oxygen, which may be obtained in the free state from bleaching-powder solution by the catalytic action of cobaltous oxide.

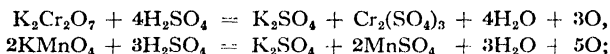
Oxidation by means of chromates or dichromates and permanganates is due to the difference in oxygen content between the acidic and basic oxides CrO_3 and Cr_2O_3, and Mn_2O_7 and $2MnO$, respectively. In the case of permanganates, however, there are several stages of reduction, thus:

$$Mn_2O_7 \longrightarrow 2MnO_3 + O \longrightarrow 2MnO_2 + 3O \longrightarrow 2MnO + 5O;$$

which become apparent more especially when the reaction takes place in alkaline solution. Thus green alkali manganate, such as Na_2MnO_4, is produced by the action of mild reducing agents in cold alkaline solution; in neutral solution, or by more vigorous reduction promoted by heating, hydrated manganese dioxide is precipitated. This substance may be further reduced if a more stable product thus results; for instance, when dilute potassium permanganate solution is added to excess of solution of alkali sulphide and free alkali, the hydrated manganese dioxide first precipitated is converted into more stable man-

ganous sulphide, the alkali sulphide being simultaneously oxidized to sulphate. In acid solution these successive stages of reduction are not so well marked, since the stable condition of soluble manganous salt is more easily reached. In some cases, however, the momentary formation of hydrated manganese dioxide can be observed; also the manganous salt formed in the reaction sometimes assists oxidation by itself becoming alternately oxidized to the dioxide and again reduced. This is the case in the oxidation of warm acidified oxalate solutions by permanganate.

Chromates and dichromates show no such intermediate stages in reduction; in acid solution chromic salts result, in neutral or alkaline solution basic chromic salts or hydrated chromic oxide itself. Owing to their great oxidizability, chromous salts are only produced by powerful reduction in absence of air.

Considering the oxidizing action of potassium dichromate and potassium permanganate in dilute sulphuric-acid solution, the reactions may thus be represented:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O,$$
$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O;$$

these equations being derived from the more simple expressions

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O,$$

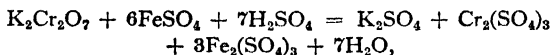
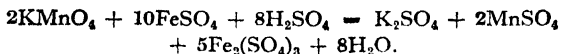
and

$$2KMnO_4 = K_2O + 2MnO + 5O.$$

The oxidation of ferrous sulphate, $FeSO_4$, to $Fe_2(SO_4)_3$ may serve as an example. Since $2FeO + O = Fe_2O_3$, the complete equations become:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O,$$

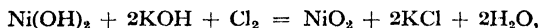
and

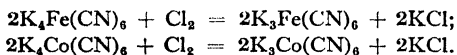
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

Both of these reagents liberate iodine from potassium iodide, oxidize sulphurous to sulphuric acid, together with some

dithionic acid, $H_2S_2O_6$, in the case of permanganate, and hydrogen sulphide to water and sulphur, together with some sulphuric acid. Acidified permanganate solution likewise reacts with hydrogen peroxide thus: $H_2O_2 + O = H_2O + O_2$, and oxidizes oxalic acid thus: $H_2C_2O_4 + O = H_2O + 2CO_2$. The complete equations for these reactions, when occurring singly, may be constructed according to the principle illustrated above.

Permanganic acid is less stable, and therefore more likely to bring about oxidation than chromic acid. This distinction is seen in the different rates with which the two substances oxidize hydrogen sulphide, and in their different behaviour towards hydrochloric acid. Both can oxidize this substance, causing chlorine to be evolved, but whilst considerable concentration and heat are necessary in the case of chromic acid, permanganic acid slowly oxidizes cold dilute hydrochloric acid solution.

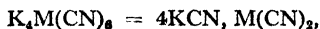
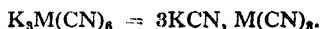
Chlorine may oxidize, either by direct union, as in the conversion of ferrous into ferric chloride, $2FeCl_2 + Cl_2 = 2FeCl_3$; or by causing the addition of oxygen or other electro-negative radicles, as, for instance, in the conversion of nickelous hydroxide into hydrated nickel dioxide in presence of alkali,

$$Ni(OH)_2 + 2KOH + Cl_2 = NiO_2 + 2KCl + 2H_2O,$$

a reaction identical with that effected by hypochlorite. Oxidation may, however, consist in the removal of hydrogen or a metal, as in the conversion of ferro- into ferri- and cobalto- into cobalti-cyanides:

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl;$$
$$2K_4Co(CN)_6 + Cl_2 = 2K_3Co(CN)_6 + 2KCl.$$

These reactions, however, really consist in the change of ferrous and cobaltous into ferric and cobaltic compounds, since

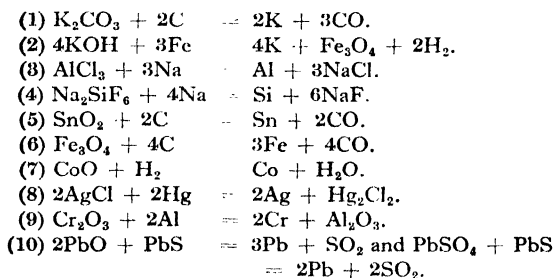
$$K_4M(CN)_6 = 4KCN, M(CN)_2,$$

and

$$K_3M(CN)_6 = 3KCN, M(CN)_3.$$

Silver oxide acts as an oxidizing agent in those cases in which it is reduced to metallic silver. Among the best-known examples are the oxidation of tartrates, formates, and glucose in solution, with the precipitation of a silver mirror on the sides of the containing vessel.

Reduction in the Dry Way

Reduction reactions carried out in the dry way are of great importance in the isolation of free elements, and in particular the metals. Typical cases are indicated by the following equations:

(1) $K_2CO_3 + 2C = 2K + 3CO$.
(2) $4KOH + 3Fe = 4K + Fe_3O_4 + 2H_2$.
(3) $AlCl_3 + 3Na = Al + 3NaCl$.
(4) $Na_2SiF_6 + 4Na = Si + 6NaF$.
(5) $SnO_2 + 2C = Sn + 2CO$.
(6) $Fe_3O_4 + 4C = 3Fe + 4CO$.
(7) $CoO + H_2 = Co + H_2O$.
(8) $2AgCl + 2Hg = 2Ag + Hg_2Cl_2$.
(9) $Cr_2O_3 + 2Al = 2Cr + Al_2O_3$.
(10) $2PbO + PbS = 3Pb + SO_2$ and $PbSO_4 + PbS = 2Pb + 2SO_2$.

A large number of well-known metallurgical operations are included in the above reactions. Reaction (9), which is applicable to ferric as well as chromic oxide, is known as Goldschmidt's reaction; it proceeds spontaneously when started by means of a fuse, on account of the large amount of heat developed in the process.

Reduction in Solution

A large number of reductions take place in solution.

The action of nascent hydrogen is illustrated in the reduction of ferric to ferrous salts by the abstraction of Cl' or SO''_4; of chlorates and nitrates to chlorides and nitrites or lower compounds, by zinc and dilute acids; and in the reduction of organic compounds by such reagents as zinc dust and water or

acid, tin and hydrochloric acid, sodium and aluminium amalgams, and sodium and amyl alcohol.

Reducing salts and analogous compounds operate by virtue of their conversion into compounds of higher electro-negative content; for instance, $SnCl_2$ to $SnCl_4$ and $FeCl_2$ to $FeCl_3$; or else by their conversion into a more highly oxygenated salt. Thus sulphurous acid and sulphites are oxidized to sulphuric acid and sulphates by the reduction of ferric salts, nitric acid, and iodic acid with liberation of iodine.

The hydrides enumerated in the list of reducing agents act in consequence of their instability, or of the superior affinity of their hydrogen for oxygen or chlorine. Hydriodic acid and hydrogen sulphide represent the two classes respectively; thus:

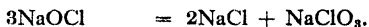
$$2HI = I_2 + 2H$$
$$H_2S + O = H_2O + S.$$

An interesting case of reduction, which has already been mentioned, is that of the mutual decomposition of two oxidizers, the evolution of oxygen resulting. Thus hydrogen dioxide and ozone decompose one another, $H_2O_2 + O_3 = H_2O + 2O_2$; and hydrogen dioxide and acidified permanganate, as before observed.

Simultaneous oxidation and reduction of a single substance is a phenomenon of common occurrence; and since the oxidation is effected by the substance itself, it may be termed " self-oxidation ". This process is illustrated by the following reactions. When hypochlorites are heated in solution, chlorides and chlorates result, the chlorate being an oxidation product of the hypochlorite, and formed by combination with oxygen derived from another portion of the hypochlorite; thus:

$$2NaOCl = 2NaCl + 2O$$
$$NaOCl + 2O = NaOClO_2,$$

or

$$3NaOCl = 2NaCl + NaClO_3.$$

The generation of potassium perchlorate from chlorate by the action of heat may be explained by the same principle:

$$4KClO_3 = 3KClO_4 + KCl:$$

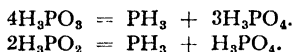
and also the formation of chlorine peroxide and potassium perchlorate by the action of sulphuric acid:

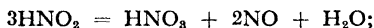
$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3$$
$$2HClO_3 = H_2O + 2ClO_2 + O$$
$$KClO_3 + O = KClO_4,$$

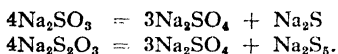
whence

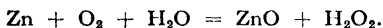
$$3KClO_3 + H_2SO_4 = K_2SO_4 + KClO_4 + 2ClO_2 + H_2O.$$

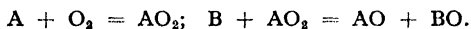
Phosphorous and hypophosphorous acids when heated give by self-reduction and oxidation phosphine and phosphoric acid,

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$
$$2H_3PO_2 = PH_3 + H_3PO_4.$$

Nitrous acid undergoes spontaneous change in aqueous solution into nitric acid and nitric oxide:

$$3HNO_2 = HNO_3 + 2NO + H_2O;$$

and alkali sulphite and thio-sulphate pass on ignition in absence of air into sulphate and sulphide and polysulphide respectively:

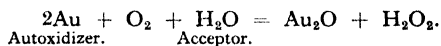
$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S$$
$$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5.$$

The phenomenon of *autoxidation* is shown when substances normally stable to oxygen are, nevertheless, oxidized in the presence of another oxidizable substance. Thus, aqueous potassium iodide is not oxidized by oxygen unless a substance such as turpentine is added. Again, zinc or lead when shaken with water in the presence of air yield hydrogen peroxide: with zinc the yield is quantitative (Traube).

$$Zn + O_2 + H_2O = ZnO + H_2O_2.$$

According to Bach, an *autoxidizer*, A, first forms an unstable peroxide which reacts with the *acceptor* B, thus:

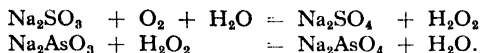
$$A + O_2 = AO_2; \quad B + AO_2 = AO + BO.$$

Thus, turpentine in the reaction above first forms a peroxide and is the autoxidizer with respect to the acceptor, potassium iodide. It may be said that the oxygen molecule is activated

and divides itself between the two substances. The reactions are concurrent, but not independent.

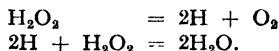
The cyanide method for gold extraction has been cited as a similar process, being basically:

$$\underset{\text{Autoxidizer.}}{2Au} + O_2 + \underset{\text{Acceptor.}}{H_2O} = Au_2O + H_2O_2.$$

In the presence of KCN, the aurocyanide $KAu(CN)_2$, is formed, whilst the hydrogen peroxide oxidizes more gold. It is highly probable, however, that such reactions with metals involve complex electrochemical processes.

Again, a reducing agent such as sodium sulphite (here called the inductor), may cause the oxidation of stable sodium arsenite (acceptor).

$$Na_2SO_3 + O_2 + H_2O = Na_2SO_4 + H_2O_2$$
$$Na_2AsO_3 + H_2O_2 = Na_2AsO_4 + H_2O.$$

The intermediate production of hydrogen peroxide may explain why water is necessary for many reactions.

Catalytic oxidation induced by the platinum metals was formerly attributed to the transient formation of oxides, but Wieland has shown that most probably hydrides are first formed. The oxidation of alcohol to acetaldehyde promoted by platinum or palladium is due to the abstraction of hydrogen by the metal, the hydrides so produced being oxidized by oxygen, regenerating the catalyst. The catalytic decomposition of hydrogen peroxide is explicable on this hypothesis by the preliminary removal of hydrogen, which is then oxidized by a further molecule of H_2O_2, thus:

$$H_2O_2 = 2H + O_2$$
$$2H + H_2O_2 = 2H_2O.$$

As we have seen, the same activation of hydrogen has been postulated to explain the reducing action of hydrogen peroxide on acidified permanganate.

CHAPTER V

GROUP I

Sub-group A		Sub-group B
	3 Li (6·94)	
	11 Na (23·00)	
19 K (39·10)		29 Cu (63·57)
37 Rb (85·45)		47 Ag (107·88)
55 Cs (132·81)		79 Au (197·2).
87 Eka-Cs —		

The typical elements, lithium and sodium, together with the three members of the A sub-group, potassium, rubidium, and cæsium, form the natural family of the alkali metals.

The existence of the highest member of the sub-group, eka-cæsium, of atomic number 87, has been reported in the uranium mineral, *samarskite* (Papish and Wainer, 1931). The alkali metals present were volatilized as halides in a stream of HCl. Fractional crystallization of chlorates and alums yielded products which gave five X-ray lines predictable for the element of atomic number 87.

The alkali metals possess one more electron than the inert gas which commences their respective periods, and the ease with which they lose this single valency electron to form univalent ions makes them the outstanding examples of electropositive elements. Nevertheless, covalent sodium methyl, $NaCH_3$, exists, and they can form chelate compounds (q.v.), as, for example, with salicylaldehyde:

$$\begin{array}{ccccc} C_6H_4 \cdot O & & & & HO \cdot C_6H_4 \\ | & \searrow & M & \swarrow & | \\ CH{=\!=}O & \nearrow & & \nwarrow & O{=\!=}CH. \end{array}$$

The anomalous behaviour of lithium, and its diagonal relationship to magnesium and II A elements should be noted.

The elements of the B sub-group, copper, silver, and gold, display very little resemblance to the metals of the alkalis, in

many respects, indeed, offering a marked contrast to them. As terminal members of transition series, however, they are seen to be related on the one hand to the metals of the eighth group, nickel, palladium, and platinum, and on the other to zinc, cadmium, and mercury, the members of sub-group II B. At the same time it may be pointed out that the divergence in properties between similarly related elements of A and B sub-groups is greatest in the extreme groups I and VII, being least in Group IV.

Since they possess atomic volumes much smaller than those of the alkali metals, there is more tendency to form covalent linkings, and, as weakly electropositive elements, they form complexes. Cupric chloride is probably $Cu[CuCl_4]$, and auric chloride betrays little saline character, being dimeric $(AuCl_3)_2$. Cuprous chloride is ionized in solution, but builds a covalent lattice in the solid state.

THE ALKALI METALS

The natural modes of occurrence of these metals suggest analogies between them. Thus lithium occurs together with sodium and potassium in certain phosphates and silicates, as well as in mineral waters and in plants; sodium and potassium occur together in felspar and other silicates, as well as in the Stassfurt deposits in the form of chlorides; rubidium and cæsium, likewise, are found in mineral waters at Stassfurt, and in silicates which may also contain lithium, sodium, and potassium. Some specimens of lepidolite, or lithia mica, contain all the alkali metals. Whilst sodium and potassium compounds are abundant, lithium compounds are somewhat, and rubidium and cæsium compounds very rare. The metals are obtained by the electrolysis of their chlorides or hydroxides, by heating their anhydrous chlorides with calcium, or, with the exception of lithium, which is volatile only at high temperature, by the reduction of their oxides by heating with carbon, or such

metals as iron, aluminium, and magnesium. The following are the chief physical properties of these metals:

		Li	Na	K	Rb	Cs
Dens.	..	0·534	0·9723	0·859	1·525	1·903
At. Vol.	..	13·0	23·7	45·5	56·0	69·8
M.P. ..	..	180·1°	97·6°	62·04°	38·5°	26–27°
B.P. ..	..	Very high	742°	667°	696°	670°

The metals and their salts colour the Bunsen flame and give spectra which contain few lines. Since the same spectra are obtained from the metals and their salts, it is concluded that the latter are dissociated in the flame.

A comparison of these physical properties reveals important gradations from lithium to cæsium. These metals are characterized by low densities and increasingly high atomic volumes, so that they stand at the apices of the atomic volume curve of Lothar Meyer. Mendeléeff rightly attributed the chemical activity of these elements to their large atomic volumes, but considered that the interspaces between the atoms in the solids were large when compared with the size of the atoms themselves. The atoms of these elements, however, are themselves large, the single valency electron being lost more readily in chemical reaction as the atomic volume increases from lithium to cæsium.

The most striking chemical property of these metals is the affinity which they manifest for oxygen. This is illustrated by the difficulty of reduction of the oxides, but more especially by the fact that the metals tarnish when exposed to air, and decompose water with evolution of hydrogen. Owing to its high melting-point lithium does not fuse under these circumstances; sodium, however, fuses; and potassium, rubidium, and cæsium, owing to the superior heat of their reaction with water, cause inflammation of the evolved hydrogen.

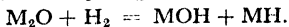
The relative degrees of electropositiveness of the alkali metals are indicated by the lowest temperatures at which they react with water. These are:

Na −98°, K −105°, Rb −108°, Cs −116°.

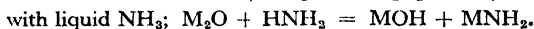
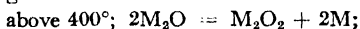
Oxides (M'_2O) and Hydroxides ($M'OH$)

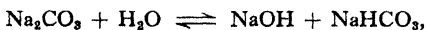
The **typical oxides,** M_2O, of the alkali metals are crystalline solids deepening in colour from lithium oxide, which is white, to cæsium oxide, which is orange-red. Lithium oxide is obtained by heating the hydroxide in a current of hydrogen; the others by partial oxidation of the metal in pure oxygen, the remaining metal being distilled off in a vacuum.

They react with water to form the hydroxides, and, excepting lithium oxide, with hydrogen thus:

$$M_2O + H_2 = MOH + MH.$$

The following reactions are also characteristic:

above 400°; $2M_2O = M_2O_2 + 2M$;

with liquid NH_3; $M_2O + HNH_2 = MOH + MNH_2$.

The hydroxides are deliquescent, except lithium hydroxide, and form crystalline masses whose aqueous solutions are strongly alkaline, and readily absorb carbon dioxide from the air. These properties are those of typically basic oxides and hydroxides, which show no acidic properties whatever; and associated therewith are certain characteristic properties of salts. Alkali halides and sulphates do not undergo hydrolysis, so that their aqueous solutions are neutral in reaction.* Solutions of such salts as the phosphates, carbonates, and borates, derived from weaker acids, are alkaline in reaction, hydroxyl ions preponderating after hydrolysis on account of the superior electrolytic dissociation of the base over the acid. Even a solution of Na_2HPO_4 is alkaline on this account, and a solution of Na_2CO_3 is hydrolyzed thus:

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3,$$

the NaOH producing a preponderance of hydroxyl ions. It is doubtful, indeed, whether the solution of any normal phosphate, carbonate, or borate possesses a neutral reaction, salts of these acids and less powerful bases being generally insoluble in water.

Another characteristic of the alkali metals depending upon

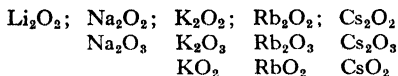
* Lithium chloride is somewhat hydrolyzed by water.

their powerfully basigenic properties is their power of forming stable acid salts, such as $M{\cdot}HSO_4$ and $M{\cdot}HCO_3$. The properties of bicarbonates are specially instructive, since those of the alkalis alone exist in the solid state, though the alkaline earth and magnesium bicarbonates are known in solution. The solid alkali bicarbonates show progressive stability from sodium to cæsium.* Even the alkali bicarbonates are decomposed by boiling water, as also are those of the alkaline earths and magnesium. The power to form bicarbonates is possessed only by the most powerful metals; normal carbonates, indeed, are formed by comparatively few metals, so great is the tendency for carbonic dioxide to be lost and a basic carbonate to be produced. The alkali metals do not form basic carbonates or any basic salts, their oxides being sufficiently basic to retain the full complement even of the weakest acid.

SUB-OXIDES AND SUB-SALTS, PEROXIDES

Various **sub-oxides**, such as Na_4O and K_4O, have been described, but their existence is doubtful. The **sub-chlorides** Na_2Cl and K_2Cl are said to be greyish-blue in colour; the blue colour of certain naturally occurring specimens of sodium chloride is attributed to the presence of sub-chloride. These compounds are possibly formed by heating the metals with the chlorides in a stream of hydrogen, or by the electrolysis of the fused chlorides themselves; but the products may be merely solid solutions of metal in the chloride.

The following **peroxides** are known:

Li_2O_2;	Na_2O_2;	K_2O_2;	Rb_2O_2;	Cs_2O_2
	Na_2O_3	K_2O_3	Rb_2O_3	Cs_2O_3
		KO_2	RbO_2	CsO_2

Sodium peroxide, Na_2O_2, is formed when sodium is ignited in a stream of oxygen. It is a yellowish-white solid which forms with water the crystallohydrate $Na_2O_2, 8H_2O$. It is a true peroxide, and possesses a constitution analogous to that

* Caven and Sand, *Chem. Soc. Trans.* (1911), **99**, 1359; (1914), **105**, 2752.

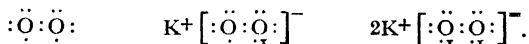
of hydrogen peroxide, since it yields this substance, together with sodium hydroxide, when dissolved in water.

When sodium peroxide is acted on by a solution of hydrogen chloride in alcohol, or with absolute alcohol at 0°, the following reaction takes place:

$$Na_2O_2 + C_2H_5OH = C_2H_5ONa + NaO \cdot OH,$$

the latter substance remaining as a white powder, known as sodium hydroperoxide. Although decomposed by mineral acids, this substance combines with acetic acid to form the sodium salt of peracetic acid, $NaOOCOCH_3$.

Potassium superoxide, KO_2, is formed when potassium is ignited in oxygen: in liquid ammonia solution potassium reacts with oxygen to form successively K_2O_2, K_2O_3 and KO_2. With water this remarkable orange-yellow superoxide yields potassium hydroxide, hydrogen peroxide and oxygen. It was formerly formulated as K_2O_4. Since, however, it possesses the same crystal structure as calcium carbide, CaC_2, it must be related to K_2O_2 and to the oxygen molecule in the following way:

$$:\ddot{\underset{\cdot}{O}}:\ddot{\underset{\cdot}{O}}: \qquad K^+\left[:\ddot{\underset{\cdot}{O}}:\ddot{\underset{\cdot x}{O}}:\right]^- \qquad 2K^+\left[:\ddot{\underset{\cdot x}{O}}:\ddot{\underset{\cdot x}{O}}:\right]^{=}.$$

The paramagnetism and the colour of KO_2 are attributed to the unpaired electron on one oxygen atom, whereas K_2O_2 is almost white. The red oxide K_2O_3 is presumably a mixed peroxide containing both anions O_2^- and $O_2^{=}$. Only the larger Group IA cations form superoxides of the type $M^+O_2^-$.

Potassium ozonate,* $(KOH)_2O_2$, is said to form when potassium hydroxide reacts with ozone. Its structure is uncertain, and it forms no hydrogen peroxide with water.

Ammonium peroxide and **ammonium hydroperoxide,** $(NH_4)_2O_2$ and $(NH_4)O{\cdot}OH$ respectively, are formed by the action of ammonia on a cold ethereal solution of anhydrous hydrogen peroxide. They are colourless, crystalline substances which decompose at ordinary temperature.

* W. Traube, *Ber.* (1916), **49**, 1670.

Halides

The following are the solubilities of the halides in 100 parts of water at about 15°:

	Li	Na	K	Rb	Cs
F′	0·27(18°)	4 $NaHF_2$ diff. sol.	+ $2H_2O$ 92·3 (18°) KHF_2 easily sol.	very sol.	366·5
Cl′	80·7 (18°)	36	33·4	91·1(20°)	186·5 (20°)
Br′	150 (deliq.)	90·3 (20°)	63	105	123·4
I′	160 (deliq.)	179 (20°)	140	150	66·3

When these salts are anhydrous they crystallize in cubes. It may be observed first that the fluorides differ from the other halides in solubility; lithium fluoride, like the alkaline earth fluorides, is almost insoluble, and sodium fluoride is but slightly soluble in water; potassium fluoride contains water of crystallization, and sodium and potassium fluorides form the acid salts $NaHF_2$ and KHF_2, which are derivatives of the double hydrofluoric acid molecule, H_2F_2. Many other examples of the exceptional properties of fluorides will be observed later. There is an increase in solubility in each case except that of cæsium, in passing from the chlorides through bromides to iodides; it may also be observed in each case that a diminution in solubility from the lithium through the sodium to the potassium halide is followed by a rise to the rubidium, and generally to the cæsium salt. These variations in solubility serve to differentiate the " typical " elements lithium and sodium from potassium, rubidium, and cæsium, which are placed at the heads of three long periods, since a break in the sequence of solubilities occurs in each case at potassium.

The solubilities of the chlorides in alcohol follow the same order as their solubilities in water. Lithium, rubidium, and cæsium chlorides, which are very soluble in water, also dissolve in alcohol; sodium and potassium chlorides, which are less soluble in water, are practically insoluble in alcohol. Sodium and potassium iodides, which are more soluble in

water than the chlorides, are also somewhat soluble in alcohol. The resemblance between lithium and magnesium and calcium is shown in the extreme solubilities of the halides, and in the fact that lithium chloride solution, when evaporated, undergoes hydrolysis in the sense of the equation

$$LiCl + HOH \rightleftharpoons LiOH + HCl;$$

on account of the loss of hydrochloric acid and the solubility of lithium hydroxide, an aqueous solution of the residue obtained by evaporation to dryness is alkaline.

In contrast with the solubilities of the simple halides, the **complex halides** of the alkalis decrease in solubility from lithium to cæsium. An example of this is seen in the case of the platinichlorides, whose solubilities in water are as follows:

$M^{\cdot}_2PtCl_6$	Li	Na	K	Rb	Cs
sol. at 10°.	easily sol.	easily sol.	0·90	0·154	0·05

The same diminution in solubility, with increase in basigenic properties of the metal, is observable with other complex salts. For instance, rubidium and cæsium can be separated from potassium by reason of the slight solubility of the stannichlorides, Rb_2SnCl_6 and Cs_2SnCl_6; and cæsium can be separated from rubidium by the precipitation of the antimonochloride, $3CsCl, 2SbCl_3$, the corresponding rubidium compound being soluble in water. When it is considered that magnesium and the alkaline earth metals, together with lithium and sodium, do not form insoluble complex halides like those formed by potassium, rubidium, and cæsium, it appears that the formation of such compounds is confined to the most electro-positive or basigenic of the elements only, the insolubility likewise increasing with increasing electro-positiveness.

Another characteristic of the alkali metals is the formation of **polyhalides.**

It is well known that iodine is more soluble in potassium-iodide solution than in water. This is due to the formation in solution of potassium polyiodides, e.g. KI_3, which may be

isolated in the form of almost black, needle-shaped crystals. This compound is evidently not very stable, since the two atoms of iodine are removed from it by the action of sodium thiosulphate. It is, however, a true "atomic" and not a "molecular" compound, since it has been shown that its solution contains the ions K^+ and I'_3. Its constitution may therefore be represented as

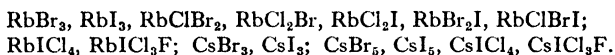
$$K^+[I—I—I]^-$$

in which the potassium atom still remains univalent. The anion is probably linear as in NH_4I_3 (Mooney, 1935).

Compounds such as $LiICl_4$ and $KICl_4$ are likewise known; they are derived from ICl_3 and the metal chloride.

In the case of rubidium and cæsium a large number of these salts are known, which crystallize well and are more stable than the potassium salts.

The following are the best known:

$RbBr_3$, RbI_3, $RbClBr_2$, $RbCl_2Br$, $RbCl_2I$, $RbBr_2I$, $RbClBrI$; $RbICl_4$, $RbICl_3F$; $CsBr_3$, CsI_3; $CsBr_5$, CsI_5, $CsICl_4$, $CsICl_3F$.

Some theoretical explanation of these remarkable compounds should be given; for unless the alkali metals are supposed to be polyvalent in them—and there is no reason to suppose this to be the case—the combination of the monohalide with free halogen is a phenomenon whose significance should be of interest.

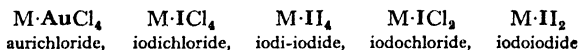
It is difficult to say how far these polyhalides retain their individuality in solution, or whether the majority exist only in solid form, sometimes akin to solid solution. When concentrated solutions of iodine in aqueous potassium iodide equivalent to a higher polyiodide are diluted, iodine separates until the contents correspond to the tri-iodide. Dawson has shown that iodine in solution in an organic solvent such as nitrobenzene dissolves potassium iodide, which is insoluble in the pure solvent, this being due to formation of KI_3 or KI_9. It seems, therefore, to be a function of the iodide ion in

potassium iodide to combine with iodine, even under conditions where no electrolytic dissociation can be assumed. This tendency is more powerful with rubidium and cæsium, as is shown by the existence of the numerous, less soluble, and more stable polyhalides of these metals. From the chemical viewpoint, therefore, polyhalide formation might be attributed to the intense electropositiveness and large ionic volume of the alkali metals, which thus may have the power of conferring basic and polyvalent properties on the halogen atoms with which they are combined.

At the same time the increase of ionic volume, coupled with the electropositiveness of the metal, might well facilitate the building of complex ions into a more stable crystal lattice with better crystallizing power.

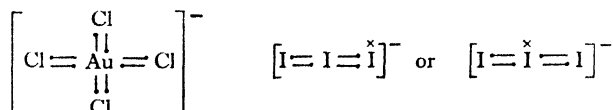
Comparable polyhalides exist in tetra-ethylammonium tri- and penta-iodides, $(C_2H_5)_4NI_3$ and $(C_2H_5)_4NI_5$, which are obtained by adding iodine to an aqueous solution of tetra-ethylammonium iodide. Ammonium tri-iodide is isomorphous with the alkali tri-iodides. The effect of increased volume of a radicle is shown by the fact that $[Co(NH_3)_6]^{+++}$ forms a polyiodide, but not Co^{+++}.

It was Werner's suggestion that such compounds are analogous to complex halides, e.g. to the aurichloride $MAuCl_4$, a halogen atom taking the place of an atom of gold thus:

$M{\cdot}AuCl_4$	$M{\cdot}ICl_4$	$M{\cdot}II_4$	$M{\cdot}ICl_2$	$M{\cdot}II_2$
aurichloride,	iodichloride,	iodi-iodide,	iodochloride,	iodoiodide

The assumption that the more electropositive halogen constitutes the nucleus of a mixed polyhalide ion is confirmed by the crystal structure of $Cs[ICl_2]$. The stability is enhanced the heavier the component halogens are (there are no trichlorides known), and at least one heavy atom, e.g. I or Br, must be present. The fact that fluorine can participate is noteworthy.

On the electronic basis the $[AuCl_4]^-$ ion results by the co-ordination of a chloride ion with neutral covalent $AuCl_3$.

In a similar fashion the I_3^- ion may be written as below, bearing in mind that its formation results by union of iodide ion with molecular or atomic iodine (only the linking electrons are shown; the iodine atom marked ($^\times$) indicates an iodide ion originally).

$$\left[\begin{array}{ccc} & Cl & \\ & \| & \\ Cl = & Au & = Cl \\ & \| & \\ & Cl & \end{array}\right]^- \qquad [I = I = \overset{\times}{I}]^- \text{ or } [I = \overset{\times}{I} = I]^-$$

In the case of the ion $[I_3]^-$ either method of representing the union achieves the same result: the linking atom is abnormal in that its valency group now contains two electrons more than its normal octet, this excess arising either by co-ordination or by covalent linkages. The complex bears a negative charge due to inclusion of the ion, I^-. On Sidgwick's views, a valency group of more than eight electrons is possible for iodine, provided all are utilized in the same fashion, i.e. if it is a " pure " valency group. Here the group is " mixed ", two of the ten electrons performing no linking function and behaving therefore as part of the atomic core; they form an " inert pair ".

Sulphates

The following are the solubilities in 100 parts of water at 18° of the **anhydrous sulphates** of the alkali metals:

Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
34·6	16·9	10·7	44·7	163·5

The order of solubility is the same as in the case of the chlorides, differentiation between metals in the typical and in the long periods being shown. Lithium sulphate often crystallizes with 1 H_2O and sodium sulphate with 7 or 10 H_2O; the other sulphates are anhydrous. Acid sulphates, $MHSO_4$, are known in each case, that of lithium being the least stable.

It was observed in the case of the chlorides that double

or complex salts show an order of solubility which is the reverse of that of the simple salts; the same is true of the double sulphates known as **alums**, $M^{\cdot}_2SO_4, R^{\cdot\cdot\cdot}_2(SO_4)_3, 24H_2O$, which show an increase in stability and insolubility with increase in basigenic properties of the alkali metal. Lithium sulphate has been shown to form an alum; sodium alum is very soluble in water and difficult to obtain in a pure, crystalline condition; potassium alum is well known; rubidium alum is much less soluble than the potassium compound, and nearly four times as soluble as cæsium alum; cæsium may be separated from rubidium by reason of these different solubilities. The following are the solubilities at 17°:

Na-	K-	Rb-	Cs- Alum
about 51	13·5	2·27	0·619

The solubility of ammonium alum is 13·7 at 20°.

The stability of alums, as well as of other double and complex salts, undoubtedly depends upon the magnitude of the difference of basigenic property between the metals of the constituent simple salts; and this is illustrated in the alums by the increase of stability from lithium to cæsium. A distinction is generally drawn between double and complex salts in the sense that whilst the former are decomposed into their constituent simple salts in solution, the latter preserve their identity in solution, giving rise to complex ions. The alums and some other double sulphates, such as $K_2SO_4, MgSO_4, 6H_2O$, are then considered to belong to the class of double salts which break up in solution, whilst the platinichlorides and ferro- and ferricyanides are complex salts, yielding complex ions in solution. This distinction, however, is not a rigid one. For whilst solutions of the alums are regarded as containing no complex ions, there are sulphates containing two metals which yield complex ions in solution. Examples of these are:

Potassium thorium sulphate	Potassium iridium sulphate
$Th(SO_4K)_4$	$Ir(SO_4K)_3$.

A concentrated solution of $CuSO_4$, K_2SO_4, 6 H_2O also contains the complex anion* $[Cu(SO_4)_2]''$. The difference, therefore, between double and complex salts is in degree rather than kind.

CARBONATES, NITRATES, PHOSPHATES, AND SULPHIDES

The solubilities of the **carbonates** and **bicarbonates** in water and alcohol are given in the following table, as far as data are available:

	Li	Na	K	Rb	Cs
$M^{\cdot}_2CO_3$ in water	1·33 (at 20°)	21·4 (at 20°)	112 (at 20°)	very sol. and deliq.	very sol. and deliq.
$M^{\cdot}HCO_3$ in water	5·5 (at 13°)	9·84 (at 20°)	26·9 (at 20°)	sol. not deliq.	sol. not deliq.
$M^{\cdot}_2CO_3$ in alcohol at atm. temp.	insol.	insol.	?	0·74	11·1

It is instructive to observe that lithium resembles the alkaline earth metals, not only in the slight solubility of its carbonate in water, but also by the fact that its bicarbonate is more soluble than its carbonate, which is the reverse of what obtains with the other alkali metals.

The **nitrates** and **phosphates** of the alkalis need but brief mention in a comparative treatment.

Lithium and sodium nitrates are very soluble in water, potassium and rubidium nitrates rather less, and cæsium nitrate sparingly soluble. Lithium and sodium nitrates are isomorphous; potassium nitrate is dimorphous, one of its forms being isomorphous with the foregoing; rubidium and cæsium nitrates combine with nitric acid, forming acid nitrates.

Lithium phosphate is nearly insoluble in water, like the alkaline earth phosphates; sodium and potassium phosphates show little resemblance to one another; there is no potassium compound, for instance, corresponding with the well-known sodium salt Na_2HPO_4, $12H_2O$.

Sulphides are obtained in the dry way by the reduction of sulphates by heating with charcoal, or by fusion of sulphur

* Rieger, *Zeit. Elektrochem*, (1901), 7, 863, 871.

with alkali carbonate. These products, however, contain polysulphides and thiosulphates. When alkali hydroxide solution is saturated with hydrogen sulphide, hydrosulphide is formed, and in the case of potassium the crystallized compound $2KSH, H_2O$ may be obtained from the solution. By the addition of an equivalent of alkali the normal sulphide is produced, the crystalline salts $Na_2S, 9H_2O$ and $K_2S, 5H_2O$ having been isolated. Anhydrous Na_2S has been prepared, as a buff powder, by the gradual heating of NaHS, and removal of the evolved hydrogen sulphide. These compounds, when dissolved in water, yield alkaline solutions owing to hydrolysis, and quickly undergo atmospheric oxidation, the first result being the liberation of sulphur which by combination with sulphide forms yellow polysulphides, this being followed by further oxidation to thiosulphate, the solution again becoming colourless. In the case of sodium the solid polysulphides Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5 are known.

Ammonium sulphide, $(NH_4)_2S$, and hydrosulphide, NH_4HS, are formed as colourless crystalline compounds when their constituent gases, well cooled, are brought together in the right proportions. They also separate from concentrated aqueous solution at low temperature. On exposure to air they turn yellow, owing to formation of polysulphides, which are probably similar in composition to the sodium compounds.

Colourless ammonium hydrosulphide solution turns yellow from the same cause; in this case, owing to loss of ammonia, sulphur and water, together with some ammonium thiosulphate, $(NH_4)_2S_2O_3$, eventually remain.

SUMMARY

Many of the facts brought forward in the above study of the salts of the alkali metals reveal a gradation of properties in accordance with the increase in atomic number from member to member, as well as a modification in properties in

passing from the typical elements lithium and sodium to the members of the long periods, potassium, rubidium, and cæsium.

Tutton has shown that the morphological and physical properties of the crystals of the various salts of potassium, rubidium, and cæsium—such properties as solubility in water, molecular volume, refractive indices, and general optical properties—follow the order of progression of the atomic weights of these metals.

The position of **ammonium** in the series of the alkali metals may be remarked upon. It is well known that the salts of the radicle (NH_4) are analogous to the salts of the alkalis as regards isomorphism and solubility. Tutton has shown* that the properties of ammonium salts are closely related to those of rubidium compounds, and that ammonium stands between rubidium and cæsium in the series of the alkali metals. The following relative values for the molecular volumes of the sulphates illustrate this statement:

	Mol. Vol.
Potassium sulphate	65·33
Rubidium ,, ...	73·77
Ammonium ,, ...	74·63
Cæsium ,, ...	85·17

It is remarkable that the molecules of ammonium sulphate occupy almost the same volume as those of the rubidium salt, although they contain eight more atoms. The explanation of this phenomenon in terms of the modern view of the structures of atoms and molecules is that the addition of four hydrogen atoms to the nitrogen atom is the addition only of four protons, with their accompanying four electrons, which go to complete the octet of the sheath of the nitrogen atom. It is not then surprising to find that the diameter of the $(NH_4)^+$ ion (2·86 A.U.) is comparable in size with that of the rubidium ion (2·98 A.U.), which contains two or three more shells of electrons than the N atom in $(NH_4)^+$.

* *Chem. Soc. Trans.* **83** (1903), 1049.

COPPER, SILVER, AND GOLD

It was stated in the introduction to this group that these three metals which form sub-group I B are related on the one hand to nickel, palladium, and platinum, and on the other to zinc, cadmium, and mercury. This relationship is shown in the following table:

Ni (58·69)	Cu (63·55)	Zn (65·38)
Pd (106·7)	Ag (107·88)	Cd (112·40)
Pt (195·2)	Au (197·2)	Hg (200·6)

This is an illustration of the rule that the properties of an element are the mean of those of its atomic analogues, that is, of adjacent elements in series and in group; thus the atomic analogues of silver are palladium, cadmium, copper, and gold.

In the study, therefore, of the elements copper, silver, and gold, the relationships thus suggested may be looked for, as well as slight similarities to the alkali metals which are the analogous members of sub-group I A.

The densities, atomic volumes, and melting-points of these elements are as follows:

	Cu	Ag	Au
Dens.	8·93	10·49	19·265
At. Vol. ..	7·12	10·29	10·23
M.P.	1085°	960·5°	1062°

It is thus observed that the atomic volumes are relatively small, the elements occurring near the minima of the atomic-volume curve; and whilst it was found that the possession of large atomic volume in the case of the alkali metals is associated with great chemical activity and affinity for oxygen, the contrary property possessed by copper, silver, and gold is connected with comparative inertness and weak power of combination with oxygen. Moreover, the affinity for oxygen is found to diminish with rising atomic number from copper to

gold, as well as from nickel to platinum, and from zinc to mercury. A gradation is observable in the reducibility of copper, silver, and gold solutions, for whilst cuprous oxide is precipitated from alkaline cupric solutions by glucose, the metals are precipitated from silver and gold solutions by this reagent; and ferrous sulphate precipitates gold, and less readily silver, but not copper from solution. As was pointed out in Chapter II, this diminution in chemical activity with rise of atomic number, which is confined to the elements of Groups VIII, I B and II B, is associated with a diminution in electro-positiveness according to the electro-potential series.

As regards the melting-points of these metals, it may be observed that whilst the figures do not show a gradation among themselves, the metals form a link between the high melting members of the eighth group and the fusible metals of Group II B. For instance, nickel melts above 1400°, and zinc at 433°, whilst the melting-point of copper lies about midway between these two. Each of these metals may be obtained, like platinum, in a colloidal form, apparently soluble in water, by forming the electric arc between terminals of the metal under water, and also by reducing their salt solutions by suitable reagents. The difference between the colloidal and ordinary forms is clearest in the case of silver; solid, variously coloured modifications, which do not conduct the electric current, being obtainable.

The physical properties of these elements, as well as their chemical properties, as manifested by their comparative stability towards air, water, and some acids, show them to be analogous to the members of the eighth group, with which they are sometimes classed. Unlike the alkali metals, they exhibit polyvalency of the transitional type, though silver is reluctant to assume bivalency. Nevertheless, as will be seen, some relationship with the alkali metals is maintained in the compounds of lower valency.

OXIDES OF THE TYPE M_2O AND THEIR SALTS

Cuprous oxide, Cu_2O, silver oxide, Ag_2O, and aurous oxide, Au_2O, stand in the order of decreasing stability. **Cuprous oxide** is the most stable oxide of copper at high temperature, being formed by heating copper or cupric oxide to a white heat in air; silver oxide loses its oxygen between 250° and 300°; and aurous oxide at 250°. The hydroxides do not exist as definite solid compounds. Hydrated cuprous oxide is precipitated as a yellow powder of variable composition which easily loses water, when alkali-hydroxide solution is added to a cuprous salt, the oxide, however, being formed when an alkaline cupric solution is reduced by glucose or an arsenite.

Silver oxide, precipitated as a chocolate-coloured powder from a silver salt by an alkali, is somewhat hydrated and slightly soluble in water, giving an alkaline reaction, but the hydroxide cannot be said definitely to exist.

Aurous hydroxide is unknown, but the violet powder formed by adding alkali to a solution of an aurous salt forms a violet liquid with water in which **aurous oxide** is contained in colloidal suspension. Cuprous and silver oxides, when precipitated by dilute ammonia, dissolve in excess of the reagent, forming hydroxides of the basic radicles $[M(NH_3)]^{\cdot}$ or $[M(NH_3)_2]^{\cdot}$. When a solution of silver oxide in ammonia is evaporated by exposure to the air, or when alcohol is added to the solution, silver nitride, Ag_3N, known as fulminating silver on account of its explosive properties, is precipitated.

Halides.—Although the salts CuCl, AgCl, and AuCl are insoluble in water, the first two at least may be obtained crystallized in cubes isomorphous with the chlorides of the alkalis. **Cuprous chloride** is volatile, and its vapour density corresponds with the molecular formula Cu_2Cl_2; in dilute solution in quinoline and other solvents, however, the molecule is CuCl, so that the cuprous ion is Cu^+ and not Cu_2^{++}. The cubic lattice of **silver chloride** is built of Ag^+ and Cl^- ions. **Aurous chloride** is probably a covalent dimer, $(AuCl)_2$.

Cuprous chloride is hydrolyzed by excess of water. It does not produce cupric chloride and copper according to the ionic reaction $2Cu^{+} = Cu^{++} + Cu$, probably on account of its insolubility. Silver chloride is stable towards water, dilute acids, and alkalis; but aurous chloride is decomposed by warm water thus:

$$3AuCl = 2Au + AuCl_3;$$

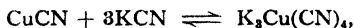
the lower chlorides of indium undergo a similar reaction, as well as some mercurous compounds.

All these monochlorides form unstable double salts with alkali chlorides; cuprous chloride dissolves in hydrochloric acid, forming probably the compound H_2CuCl_3, to which the salt K_2CuCl_3 corresponds. A solution of cuprous chloride in hydrochloric acid absorbs carbon monoxide, the compound $CO<{CuCl \atop CuCl}$ resulting. The slight solubility of silver chloride in water is perceptibly increased by the addition of hydrochloric acid. Cuprous and silver bromides and iodides are similar to the chlorides. The silver halides show progressive insolubility from chloride to iodide, for 1 litre of water at 20° dissolves

AgCl	AgBr	AgI
0·0016 g.	0·000084 g.	0·0000028 g.

All these halides dissolve in aqueous ammonia, forming ammines containing basic ions such as $[CuNH_3]^{\cdot}$ and $[Ag(NH_3)_2]^{\cdot}$. In the case of silver there is progressive insolubility from the chloride to the iodide. Silver halides also dissolve in sodium thiosulphate solution, forming the complex salt $Na_4[Ag_2(S_2O_3)_3]$.

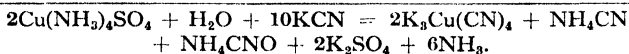
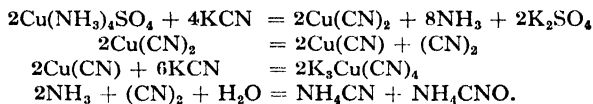
Complex Cyanides are known in the case of cuprous, silver, and aurous compounds. Cuprous cyanide dissolves in potassium-cyanide solution according to the following reaction:

$$CuCN + 3KCN \rightleftharpoons K_3Cu(CN)_4,$$

the potassium cuprocyanide produced being sufficiently stable

to resist decomposition by hydrogen sulphide in neutral or alkaline solution. The well-known analytical separation of copper and cadmium depends on this fact, since the cadmium double cyanide, $K_2Cd(CN)_4$, is decomposed by hydrogen sulphide.

The reaction is generally carried out by the addition of potassium cyanide to cuprammonium-sulphate solution, when the following changes take place:

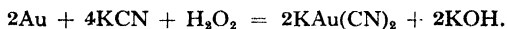
$$2Cu(NH_3)_4SO_4 + 4KCN = 2Cu(CN)_2 + 8NH_3 + 2K_2SO_4$$
$$2Cu(CN)_2 = 2Cu(CN) + (CN)_2$$
$$2Cu(CN) + 6KCN = 2K_3Cu(CN)_4$$
$$2NH_3 + (CN)_2 + H_2O = NH_4CN + NH_4CNO.$$

$$2Cu(NH_3)_4SO_4 + H_2O + 10KCN = 2K_3Cu(CN)_4 + NH_4CN + NH_4CNO + 2K_2SO_4 + 6NH_3.$$

Silver cyanide unites with potassium cyanide to form $KAg(CN)_2$, which may be obtained solid, but is decomposed by hydrogen sulphide.

Potassium aurocyanide, which may be obtained in crystals, is formed when finely-divided gold dissolves in potassium-cyanide solution in presence of air. The following reaction takes place:

$$2Au + 4KCN + 2H_2O + O_2 = 2KAu(CN)_2 + 2KOH + H_2O_2;$$

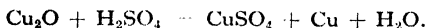
the H_2O_2 produced reacting with more gold thus:

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH.$$

These reactions form the basis of the cyanide gold process, the metal being obtained by electrolysis of the solution, or precipitation by zinc.

The three oxides of the type M_2O differ considerably in their power of forming **oxysalts.**

The only oxysalts corresponding with Cu_2O at present known are cuprous sulphite, thiosulphate, sulphate, carbonate, and oxalate; the two former of these form double salts with the corresponding alkali compounds. When cuprous oxide is acted on by dilute nitric or sulphuric acid, a solution of cupric

salt is obtained, together with metallic copper. Thus, for instance:

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

By bringing together cuprous oxide and methyl sulphate, however, in the absence of water, Recoura* obtained cuprous sulphate as a grey powder, which is immediately decomposed by water into cupric sulphate and copper.

Oxysalts corresponding to Ag_2O, such as the nitrate and sulphate, are well known, and seem to take the place of the unknown salts of the oxide AgO. Except the carbonate and borate, they are not hydrolyzed by water.

Aurous oxide, Au_2O, resembles cuprous oxide in its slight power of salt formation; the sulphite and thiosulphate are known, but the common oxysalts do not appear to exist.

Viewed from the standard of the periodic law, these three oxides present certain anomalies. Silver oxide evidently does not belong to the same category as cuprous and aurous oxides, and as regards these two oxides the former is probably the more basic, just as copper is more electro-positive than gold.

Cupric and Auric Oxides and their Salts

Cupric oxide, CuO, and its salts are well known, and require but brief treatment. When alkali hydroxide is added to cupric sulphate solution the precipitate is at first pale blue, but becomes deeper as more alkali is added. At first a basic sulphate is precipitated, but with more alkali this is supposed to be converted into the hydroxide $Cu(OH)_2$, though some authorities state that a basic sulphate still remains. The precipitate appears to be insoluble in excess of alkali, but turns nearly black when the liquid containing it is boiled. This black precipitate, which tenaciously retains alkali, has the composition $4CuO, H_2O$, but is converted into CuO when heated to redness.

If a very little copper sulphate is added to much concen-

* *C. r. de l'Acad. des Sciences*, **148**, 1105–8.

trated alkali solution the precipitate formed dissolves, forming a deep-blue solution. This may be taken as a sign of the possession of acidic properties by cupric hydroxide, but is more probably due to the colloidal state being assumed.

Cupric salts usually contain water of crystallization, and are then blue or green, being white or yellow when anhydrous. Of the **halides**, the iodide is unstable, breaking down, on formation, into cuprous iodide and iodine. The **nitrate** is decomposed on heating, leaving the oxide, thus resembling the nitrates of heavy metals, and differing from the nitrates of the members of the alkali group. The **carbonate** and **phosphate** are insoluble in water, the former always being basic; the compound $[Cu(OH)_2Cu]CO_3$ is well known in the mineral malachite. The **sulphate**, $CuSO_4$, $5H_2O$, also forms basic salts, its dilute aqueous solution being hydrolyzed by boiling, with the formation of sulphuric acid and an insoluble green basic sulphate. Basic salts are also formed when the normal sulphate is kept for several hours at a dark-red heat, as well as by fractional precipitation with alkali-hydroxide solution.

Cupric sulphate forms isomorphous mixtures with the sulphates of the metals adjacent to copper in the periodic table, that is, with zinc sulphate and the sulphates of iron, nickel, and cobalt; this notwithstanding the fact that cupric sulphate normally crystallizes with five molecules of water and all the other sulphates with seven. Whether the mixed crystals contain five or seven molecules of water depends on the proportion of cupric sulphate present.

Cupric sulphate forms double salts with the sulphates of the alkali metals, that with ammonium sulphate, $CuSO_4$, $(NH_4)_2SO_4$, $6H_2O$, being the best known. In these salts a molecule of alkali sulphate takes the place of one of water in the heptahydrated salt. These salts are isomorphous with the corresponding double salts containing ferrous iron, nickel, cobalt, zinc, and magnesium.

The blue solution obtained by adding excess of ammonia to cupric-sulphate solution contains the salt $[Cu(NH_3)_4]^{\cdot\cdot}SO_4$.

Further reference will be made to this compound at the end of Chapter XII.

Auric oxide is represented by the formula Au_2O_3, and its chloride is $AuCl_3$. Compounds of the empirical formulæ AuO and $AuCl_2$ are known, but they must be considered as aurous aurate, $Au{\cdot}AuO_2$, and chloraurate, $Au{\cdot}AuCl_4$, respectively. The existence of a sesquioxide, and compounds corresponding thereto, confers upon gold in the auric compounds more pronounced acidic properties than have hitherto appeared in this group.

Auric hydroxide, $Au(OH)_3$, is precipitated as a brown powder when potassium hydroxide is added to a concentrated solution of auric chloride; it is soluble in excess of alkali, forming aurate, $KAuO_2$, from which it is again precipitated by dilute nitric acid. When dehydrated, $Au(OH)_3$ first forms auryl hydroxide, $AuO{\cdot}OH$, and then auric oxide, Au_2O_3, which decomposes below 250° into its elements.

The **aurates,** for instance $KAuO_2$, $3H_2O$, or $KAu(OH)_4$, H_2O are well-defined crystalline salts, soluble in water, and yielding alkaline solutions which are rather unstable. Auric oxide is almost exclusively acidic in function, and forms no stable oxysalts. It is thus less basic than alumina, which forms a fairly stable sulphate.

When concentrated ammonia is added to auric oxide a substance of the empirical composition AuN_2H_3, $3H_2O$, known as fulminating gold, is produced. This compound is possibly an ammine of the composition $\left[Au\begin{matrix}(NH_3)_2\\(OH)_2\end{matrix}\right]OH$. Some salts of the tervalent tetra-ammino basic radicle $[Au(NH_3)_4]^{\cdots}$ have been prepared.*

The **trihalides** of gold present many of the properties of halanhydrides, whilst their saline qualities are very feeble. **Auric chloride,** $AuCl_3$, obtained by carefully evaporating a solution of gold in chlorine water, is a brown crystalline mass, soluble in alcohol and ether, and melting at 288°. Orange-

* Weitz, *Annalen*, (1915), **410**, 117.

red crystals, $AuCl_3, 2H_2O$, may be obtained from aqueous solution; it also forms chlorauric or aurichloric acid, $HAuCl_4, 3H_2O$, with hydrochloric acid, from which chloraurates or aurichlorides, such as $2KAuCl_4, H_2O$ are derived. Auric chloride thus resembles platinic chloride in combining with alkali chlorides to form complex alkali salts.

Auricyanides are well known, potassium auricyanide, $KAu(CN)_4$, being obtained by adding concentrated potassium-cyanide solution to a neutral solution of auric chloride. It is a colourless salt, from which white crystals of the acid $HAu(CN)_4$ can be obtained.

Sulphides

Copper forms two sulphides, Cu_2S and CuS, corresponding with cuprous and cupric oxides; **cupric sulphide** loses sulphur when heated gently out of contact with air, yielding **cuprous sulphide,** which is also produced when the metal is heated with sulphur. Both compounds occur in nature, though cuprous sulphide, like the oxide, is more stable than the corresponding cupric compound. Cupric sulphide shows very feebly acidic properties, being perceptibly soluble in alkali-sulphide solutions.

Silver forms but one sulphide, Ag_2S, a black solid insoluble in water, alkalis, and alkali sulphides. Three sulphides of gold are known, Au_2S, Au_2S_2, and Au_2S_3, the latter of which is very unstable. Aurous sulphide, Au_2S, formed by reducing a hot solution of auric chloride with hydrogen sulphide, combines with alkali sulphides, forming thioaurites, $MAuS$. The disulphide, Au_2S_2, possibly aurous thioaurate, $AuAuS_2$, is formed when hydrogen sulphide acts upon cold auric-chloride solution. It reacts with sodium sulphide, thus:

$$Au_2S_2 + 2Na_2S = 2NaAuS + Na_2S_2,$$

and combines with a polysulphide, forming thioaurate. Auric sulphide, Au_2S_3, which is thioauric anhydride, combining with alkali sulphides to form thioaurates, is not formed in the wet

way, but by passing hydrogen sulphide over a heated aurichloride.

The superior acidic properties of gold as compared with silver and copper compounds are well illustrated in the properties of the above sulphides.

Sub- and Per- Oxides

Copper suboxide, Cu_4O, is said to be formed as an olive-green powder by the reduction of an alkaline cupric solution by stannous chloride. The copper first passes through the cuprous stage, and finally separates as metal if reduction is continued. This oxide yields cuprous chloride and copper with hydrochloric acid, and may be only a mixture of cuprous oxide and copper.

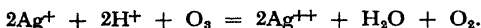
Silver suboxide, Ag_4O, possibly exists, and the subhalides Ag_2F and Ag_2Cl: but these substances are probably mixtures of metal with Ag_2O or the corresponding halide.

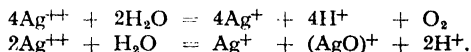
Copper peroxide, CuO_2, H_2O, is formed as a yellowish-brown crystalline powder by the action of dilute hydrogen peroxide on cupric hydroxide; it is unstable when moist, and is probably a superoxide since with dilute acids it gives cupric salts and hydrogen peroxide.

There is also an oxide, Cu_2O_3, obtained as a yellow powder when concentrated sodium hydroxide solution is electrolyzed with a copper anode.

Silver peroxide, AgO. When a neutral solution of silver nitrate undergoes electrolysis, a black powder is deposited at the anode, which contains AgO and Ag_2O_3, neither being a true superoxide. When this mixture is boiled with water, oxygen is evolved, and the oxide AgO remains.

Ozone reacts with silver nitrate in nitric acid solution to yield a black, strongly oxidizing solution of **argentic nitrate,** $Ag(NO_3)_2$.

$$2Ag^+ + 2H^+ + O_3 = 2Ag^{++} + H_2O + O_2.$$

It is unstable to water, and occasionally forms insoluble basic compounds containing tervalent silver (Noyes, 1935).

$$4Ag^{++} + 2H_2O = 4Ag^+ + 4H^+ + O_2$$
$$2Ag^{++} + H_2O = Ag^+ + (AgO)^+ + 2H^+.$$

Dark-brown **argentic fluoride**, AgF_2, is obtained when fluorine reacts with gently heated silver or its halides. Stable, coloured co-ordination compounds of bivalent silver are known, e.g. $[Ag(py)_4](NO_3)_2$; $[Ag(py)_4]S_2O_8$. (py = pyridine.)

There is thus reason to believe that AgO is a feebly basic oxide, and the analogue of cupric oxide, CuO; but in chemical properties it is similar to lead peroxide, PbO_2.

The increase of stability conferred by co-ordination may be emphasized at this stage. Ethylenediamine (en) forms stable cupric compounds of the type $[Cu2en]X_2$, where X = NO_2^-, $H_2PO_2^-$, CNS^-, I^-. Using ethylenethiourea (etu), cuprous nitrate, non-existent in the simple form, gives the stable compound, $[Cu4etu]NO_3$, and aurous nitrate gives $[Au2etu]NO_3$, this substance being unaffected by hot solvents and not reduced by formaldehyde.

CHAPTER VI

GROUP II

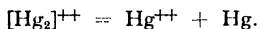
Sub-group A		Sub-group B
	4 Be (9·1)	
	12 Mg (24·32)	
20 Ca (40·07)		30 Zn (65·37)
38 Sr (87·63)		48 Cd (112·40)
56 Ba (137·37)		80 Hg (200·6)
88 Ra (226·4)		

The metals calcium, strontium, and barium of sub-group **A**, immediately following potassium, rubidium, and cæsium, respectively, in series, form a group of closely-allied electropositive elements, the metals of the alkaline earths; to these

must be added radium following in series eka-cæsium the rare alkali metal.

The metals of this sub-group have smaller atomic volumes than the alkali metals, e.g. the value for barium (39) is lower than that for cæsium (70·7). Because of this, and because of the increase of ionic charge to two units, the members display weaker electropositive character than their neighbours of Group I A.

Sub-group B, containing the metals zinc, cadmium, and mercury, is related to sub-group A in the same general manner as is I B to I A. Its members are less positive than the metals of the alkaline earths, and, as might be anticipated from the relative positions of the two sections of the group in the long series, they do not present any striking resemblances to the alkaline-earth metals. The group valency, two, is, however, characteristic, univalent mercury being only an apparent exception (see p. 88). Being elements of low atomic volume, tendencies to covalency are much in evidence, e.g. in the complex zinc compounds, the auto-complexes of cadmium, and in the weakly saline properties of the halides which reach a minimum in mercuric chloride. These halides possess low electrical conductivity. Mercury forms a large number of " organic " compounds, and mercurous salts resemble cuprous salts in that they are very susceptible to the change

$$[Hg_2]^{++} = Hg^{++} + Hg.$$

Beryllium and magnesium, the " typical " elements of the group, resemble the II B elements, though they have affinities with both sub-groups, magnesium in particular. Because of its low atomic volume beryllium shows a tendency to covalent linking. Thus, BeO has a covalent lattice, whilst MgO is ionic. The ion, Be^{++}, co-ordinates $4H_2O$ with great firmness, and many of its salts form auto-complexes. The simple acetate readily yields the complex compound $Be_4O(COOCH_3)_6$, which is soluble in organic solvents. In this molecule four BeO_4 tetrahedra possess the central " basic " oxygen atom in

common, the remaining corners having oxygen atoms from the acetate groups (Pauling, 1934).

BERYLLIUM (GLUCINUM) AND MAGNESIUM

From their positions in series, beryllium between lithium and boron, and magnesium between sodium and aluminium, it is evident that magnesium should be more electro-positive or basigenic than beryllium. That this is the case is shown by the following facts:

Beryllium hydroxide is feebly acidic, being dissolved by cold alkali hydroxides, whilst magnesium hydroxide is not so dissolved. Metallic beryllium does not combine with oxygen so readily as magnesium, nor does it so readily decompose water; moreover, it may be obtained by reducing the oxide with magnesium. Beryllium yields basic salts more readily than magnesium.

Both these metals* can be prepared from their chlorides by reduction with sodium or potassium, or by electrolysis. Both metals have a silvery lustre and low density; the density of beryllium is 1·842, and of magnesium 1·75, the atomic volumes being 4·94 and 13·90. Neither metal is easily oxidized or acted on by water; boiling water, indeed, slowly reacts with magnesium, but not with beryllium. Magnesium melts at 800° and beryllium at about 1280°. These metals are easily dissolved by dilute hydrochloric and sulphuric acids, and magnesium by nitric acid; but beryllium is scarcely acted on by nitric acid, in this resembling aluminium. Beryllium also resembles aluminium, and differs from magnesium, in being soluble in alkali hydroxides.

In the properties of the element and its compounds beryllium bears a relationship to the alkaline-earth metals similar

* Beryllium is rather scarce; beryl, $3BeO$, Al_2O_3, $6SiO_2$, is the chief mineral. The occurrence of magnesium as sulphate in Epsom-salt, $MgSO_4$, $7H_2O$, as chloride in carnallite, KCl, $MgCl_2$, $6H_2O$, as carbonate in magnesite, $MgCO_3$, and dolomite $(MgCa)CO_3$, as well as in many silicates, recalls the manner of occurrence of the alkaline-earth metals.

to that which lithium bears to the alkalis; and the relationship of beryllium in the second group to aluminium in the third is paralleled by that of boron in the third group to silicon in the fourth.

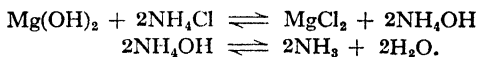
The oxides BeO and MgO are both formed by the ignition of the metals in air, as well as of oxysalts, such as the nitrates, carbonates, and sulphates, in presence of water vapour. Beryllium sulphate is, however, much more easily decomposed than magnesium sulphate, as becomes the inferior electro-positive character of the former metal. A comparison of the ease of decomposition of these oxysalts with those of the alkali and alkaline-earth metals is instructive, for, at a red heat, the sulphates of the alkaline-earth metals are not decomposed, and the carbonates of the alkalis are but slightly decomposed, whilst their nitrates, on powerful ignition, lose only oxygen, forming nitrite. After powerful ignition beryllium oxide is insoluble in acids, thus resembling aluminium oxide; magnesium oxide is not thus rendered insoluble.

The oxides of beryllium and magnesium are both produced by the gentle ignition of their **hydroxides**, and are not again readily converted into hydroxides by the action of water. Gently ignited magnesium oxide, however, is sufficiently soluble in water to give an alkaline reaction, the solution containing magnesium hydroxide. When this oxide is mixed with a little water it gradually sets to a firm mass, and with the chloride forms Sorel cement.

Magnesium hydroxide is soluble in ammonium-chloride solution, and this property finds an application in chemical analysis, ammonium chloride preventing the precipitation of magnesium hydroxide by ammonia. This fact is explained on the ionic theory by the formation of ammonium hydroxide by interaction of ammonium chloride with the small amount of magnesium hydroxide in solution in water; this ammonium hydroxide is only slightly dissociated into ammonium and hydroxide ions in solution, and some of it decomposes into ammonia and water. Thus the concentration of OH ions in

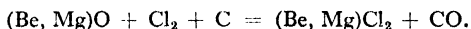
solution is diminished, and more $Mg(OH)_2$ dissolves in consequence.

The following equations illustrate these reactions:

$$Mg(OH)_2 + 2NH_4Cl \rightleftharpoons MgCl_2 + 2NH_4OH$$
$$2NH_4OH \rightleftharpoons 2NH_3 + 2H_2O.$$

At the same time the double or complex salt $(NH_4)_2MgCl_4$ is probably formed in solution, and the presence of magnesium in the anion $MgCl_4''$ would prevent its precipitation by ammonium hydroxide.

As has already been stated, $Be(OH)_2$ dissolves in cold alkali-hydroxide solutions, owing to feebly acidic properties. From these solutions a polymeric form of hydroxide separates on boiling or long standing in the cold. In this latter property beryllium hydroxide differs from zinc and aluminium hydroxides, but resembles chromic hydroxide. Magnesium hydroxide is not soluble in alkalis.

The chlorides $BeCl_2$ and $MgCl_2$ both result from the action of hydrochloric acid on the metals or oxides. They are formed in the anhydrous state by the action of chlorine on a heated mixture of the oxides with carbon:

$$(Be, Mg)O + Cl_2 + C = (Be, Mg)Cl_2 + CO.$$

Anhydrous magnesium chloride may also be prepared by igniting the hydrated chloride in a vacuum, or in a current of hydrogen chloride, as well as by evaporating a solution of the salt with excess of ammonium chloride, and heating the resulting double salt.

$BeCl_2$ crystallizes in silky needles which melt at about 600° and sublime at a somewhat higher temperature; $MgCl_2$ crystallizes in pearly leaflets, which can be melted and distilled at a red heat in an atmosphere of hydrogen.

Both salts are deliquescent, and crystallize in the hydrated forms $BeCl_2, 4H_2O$ and $MgCl_2, 6H_2O$ respectively. The hydrated salts readily yield basic compounds on warming, and

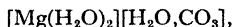
many such basic salts of beryllium of doubtful composition have been described. Beryllium chloride forms with ether the compound $BeCl_2 \cdot 2(C_2H_5)_2O$, and with ammonia a di- and tetra-ammoniate.

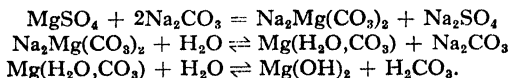
When hydrated magnesium chloride is decomposed by heat the oxychloride $Mg\begin{smallmatrix}\diagup OH \\ \diagdown Cl\end{smallmatrix}$ is formed, whilst the anhydrous chloride, when heated in moist air, yields the oxide and chlorine, $2MgCl_2 + O_2 = 2MgO + 2Cl_2$, a reaction which is employed technically in the Weldon-Pechiney chlorine-recovery process. Beryllium chloride behaves similarly. Magnesium chloride forms stable double salts with the alkali chlorides of the type $MCl, MgCl_2, 6H_2O$.*

Other Salts. Of the other salts of these metals reference may be made to the carbonates and sulphates.

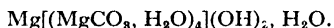
Beryllium carbonate separates in the hydrated crystalline form, $BeCO_3, 4H_2O$, from the solution obtained by passing carbon dioxide through water containing the hydroxide in suspension. This solution probably contains bicarbonate. The normal salt very easily gives off carbon dioxide, forming basic carbonate.

Magnesium carbonate is isodimorphous with calcium carbonate: it occurs as the mineral magnesite. From a solution of magnesium carbonate in carbonic acid, crystals of a trihydrate separate on standing. This may be formulated as

$$[Mg(H_2O)_2][H_2O,CO_3],$$

for it loses only two-thirds of its water in a current of air at 100°, or when heated with boiling xylene at 137°: further dehydration causes a loss of carbon dioxide. The following reactions probably take place when magnesium sulphate and sodium carbonate solutions are mixed:

$$MgSO_4 + 2Na_2CO_3 = Na_2Mg(CO_3)_2 + Na_2SO_4$$
$$Na_2Mg(CO_3)_2 + H_2O \rightleftharpoons Mg(H_2O,CO_3) + Na_2CO_3$$
$$Mg(H_2O,CO_3) + H_2O \rightleftharpoons Mg(OH)_2 + H_2CO_3.$$

* The mineral carnallite is $KCl, MgCl_2, 6H_2O$.

The initial product is a soluble double carbonate which is decomposed by water to form " magnesia alba ", a hydrated basic carbonate of varying composition. According to Menzel (1930) this product contains varying amounts of hydrated $MgCO_3$ and $Mg(OH)_2$ associated with an essential constituent in which the ratio $5MgO : 4CO_2$ is maintained under widely varying conditions—even up to 250°. When dried by liquid ammonia, or by acetone, this constituent may be written as

$$Mg[(MgCO_3, H_2O)_4](OH)_2, H_2O.$$

On standing for some days in contact with the mother liquor containing sodium carbonate, the basic carbonate changes completely into $MgCO_3, 3H_2O$ again, from which, by treatment with hot water, the above basic constituent is produced.

The metals zinc, mercury, lead, and copper are analogous to magnesium in the readiness with which they form basic carbonates. It is interesting to observe that in the case of still less basigenic elements, such as ferric iron and aluminium, the action of alkali carbonates in solution leads to the production of hydroxides only: that is, the carbonates are completely hydrolyzed by water. Sulphides are similar to carbonates in their instability, since hydrogen sulphide is an acid comparable in strength with carbonic acid. Thus magnesium, aluminium, chromic, and other sulphides are unstable towards water, being hydrolyzed with the production of metallic hydroxide and hydrogen sulphide.

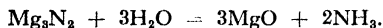
Beryllium sulphate, $BeSO_4$, generally crystallizes with four molecules of water; a heptahydrated salt is however known which is isomorphous with magnesium sulphate. This compound easily gives rise to basic salts, a number of which are known. The tendency to hydrolysis is shown by the acid reaction of the aqueous solution of the salt. When ignited strongly, crystallized beryllium sulphate loses water and sulphur trioxide, leaving a residue of the pure oxide. This reaction has been employed in determining the atomic weight of beryllium.

Magnesium sulphate usually crystallizes in rhombic prisms containing $7H_2O$, and isomorphous with zinc sulphate. It is known, however, in other forms containing amounts of water varying from 1 to 24 H_2O. The heptahydrated form can exchange one of its molecules of water for a molecule of an alkali sulphate; double salts, such as $MgSO_4$, K_2SO_4, $6H_2O$, being formed. In this it resembles zinc sulphate. No basic sulphate is known.

The sulphates of beryllium and magnesium, though less stable than those of the alkaline-earth metals, and therefore less perfect salts, differ from these by their ready solubility in water.

Beryllium, like magnesium, forms no true superoxide of the type MO_2, but instead forms a hydrated mixture of BeO and BeO_2, which is moderately stable and shows the general character of a peroxide.

Magnesium forms a **nitride**, Mg_3N_2, by direct union, when the metal is heated in nitrogen gas. This is decomposed by strong ignition in air or oxygen, and is acted upon by water, thus:

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3.$$

Lithium, which resembles magnesium in some respects, as would be expected from the periodic law, forms a similar compound.

The lattices of Mg_3N_2 and Ca_3N_2 are ionic.

CALCIUM, STRONTIUM, AND BARIUM

These elements display great similarity to one another in modes of occurrence * and properties. Reduction of the halides by sodium or potassium, or electrolysis of halides, are methods available for the isolation of the metals. Metallic calcium has been obtained in quantity by the electrolysis of fused calcium

* In addition to the minerals calcite $CaCO_3$, strontianite $SrCO_3$, witherite $BaCO_3$, anhydrite $CaSO_4$, and gypsum $CaSO_4$, $2H_2O$, celestine $SrSO_4$, heavy-spar $BaSO_4$, isomorphous mixtures or compounds occur in barytocalcite $(BaCa)CO_3$, alstonite $(BaCa)SO_4$, and barytocelestine $(BaSrCa)SO_4$.

chloride kept below 800° to prevent union of the liberated metal with $CaCl_2$ to form Ca_2Cl_2, or its combustion in air. An iron cathode just touches the surface of the electrolyte, and a rod of metal, covered with fused calcium chloride, is gradually built up as the cathode is raised during electrolysis. The product contains 97·75 per cent of calcium.

Calcium is a rather hard, silvery-white metal; its density is about 1·54, and its melting point 810°.

Pure barium distils when a mixture of baryta and silicon is heated * in an exhausted steel tube at 1200°.

These metals possess higher melting points than the alkali metals, and are less easily oxidized. They are comparatively stable in the air, but combine with oxygen and the halogens when heated with them. They decompose water with evolution of hydrogen at atmospheric temperature, though less vigorously than the alkali metals. Their chlorides are volatile in, and colour the Bunsen flame, giving spectra which differ slightly from those of the metals. The chemical activity of calcium is comparable with that of lithium, and the activity increases with increasing atomic weight through strontium to barium.

The hydroxides, carbonates, and nitrates of these metals are more easily decomposed by heat than the corresponding compounds of the alkali metals, and, moreover, in the case of calcium, the chloride is slightly hydrolyzable. This is all in accordance with the position of these elements in the periodic system.

Oxides and Sulphides

The oxides of the type MO all result from the direct union of their elements, but are usually prepared by decomposing the hydroxides, carbonates, or nitrates by heat. The ease with which these compounds are thus decomposed decreases in passing from calcium to barium. For instance, the hydroxides of strontium and barium part with water only on

* Matignon, *Compt. rend.* (1913), **156**, 1378.

being heated strongly in a current of air; calcium hydroxide, however, commences to lose water at 100°. Again, calcium carbonate is decomposed into the oxide and carbon dioxide at a low red heat, whereas a white heat is required to decompose barium carbonate. Barium oxide is best obtained by ignition of the nitrate, or by reduction of the carbonate with carbon.

As regards the effect of heat on the nitrates of groups I A and II A, it is interesting to note that it is only the alkali nitrates which yield nitrites on ignition,* the less positive elements of II A forming the oxides. In general, a nitrate other than those of group I A yields, on heating, the oxide of the metal or the metal itself.

The oxides of calcium, strontium, and barium are refractory solids; barium oxide fuses in the oxyhydrogen flame and calcium oxide can be fused in the electric furnace; the brilliant light emitted by lime when heated in the oxyhydrogen blowpipe flame is well known as the limelight.

These oxides all readily unite with water (slake), giving the hydroxides $M(OH)_2$. Lime on slaking may reach a temperature of 150°, but baryta may actually become incandescent. The greater affinity of barium oxide for water, and the greater stability of the hydroxide as compared with the calcium compound, illustrate the increase in the basigenic properties of these metals with increase in atomic number. The solubility of the hydroxides similarly increases; 100 parts of water at 15° dissolve

$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
0·127	0·57	2·89.

Calcium hydroxide is rather less soluble in hot than in cold water; the solubility of strontium hydroxide, and especially of barium hydroxide, increases rapidly with rise of temperature.

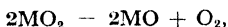
Each of these hydroxides can be obtained crystalline from its solution; $Sr(OH)_2$ and $Ba(OH)_2$ separate in isomorphous forms containing $8H_2O$.

* Silver nitrate first yields nitrite, which easily passes into metal.

Solutions of these hydroxides are powerful alkalis, having caustic properties, and readily absorbing carbon dioxide.

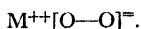
The peroxides MO_2.—When solutions of the hydroxides of calcium, strontium, and barium are mixed with a solution of hydrogen peroxide, crystals of the hydrated peroxides $MO_2, 8H_2O$ are deposited. Anhydrous barium peroxide is likewise formed on heating the monoxide in oxygen or in the air (in Brin's process in air at 700° under two atmospheres pressure), but calcium and strontium oxides do not so readily combine with oxygen.

All these peroxides lose oxygen on ignition:

$$2MO_2 = 2MO + O_2,$$

but are progressively stable from calcium to barium. When acted upon by dilute acids they yield salts of the metals and a solution of hydrogen peroxide, e.g.:

$$MO_2 + H_2SO_4aq = MSO_4 + H_2O_2aq.$$

Accepting the constitution H·O·O·H for hydrogen peroxide, these compounds are salts of hydrogen peroxide;

$$M^{++}[O—O]^{=}.$$

Their stabilities increase as the size of M^{++} increases.

The sulphides result from the action of hydrogen sulphide on the heated oxides;

$$MO + H_2S = MS + H_2O,$$

or more readily by the reduction of the sulphates by heating with carbon * or hydrogen. They are white or yellowish-white substances, which are phosphorescent; that is, they possess the power of glowing in the dark after exposure to light. Calcium sulphide is known as Canton's phosphorus, and barium sulphide, which emits an orange-coloured light, as Bononian phosphorus. Strontium sulphide emits light

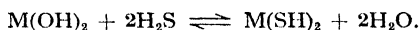
* Barium sulphide, thus produced from heavy spar ($BaSO_4$), is the starting-point for the technical preparation of the barium salts.

which varies in colour according to its manner of preparation. These phenomena are due to the presence of a trace of another sulphide, such as bismuth sulphide, known as the phosphorogen.* These sulphides are almost insoluble in, but are decomposed more or less readily by, water, with formation of hydroxide and hydrosulphide, thus:

$$2MS + 2H_2O = M(OH)_2 + M(SH)_2,$$

or, in the case of barium, the hydroxyhydrosulphide $M(OH)(SH), 5H_2O$.

The sulphides, therefore, are not precipitated by the action of hydrogen sulphide on the hydroxide solutions, but hydrosulphides result, thus:

$$M(OH)_2 + 2H_2S \rightleftharpoons M(SH)_2 + 2H_2O.$$

Calcium hydrosulphide may be obtained, crystallized with 6 molecules of water, from the solution formed by the action of hydrogen sulphide on milk of lime. When this compound is heated in a stream of hydrogen sulphide, the sulphide CaS results.

The alkaline-earth sulphides resemble the alkali sulphides in the manner in which they are hydrolyzed by water, though they differ from them by being practically insoluble in water. As was observed in the case of the alkali sulphides, and many other salts, this hydrolysis is due to the fact that a strong base is combined with a feeble acid.

It was seen in studying the alkali sulphides that they are basic, combining with acidic sulphides, such as those of arsenic and antimony, to form thiosalts. Barium sulphide similarly combines with acidic sulphides, but calcium sulphide does not.

The alkaline-earth or magnesium sulphides form a convenient source of hydrogen sulphide. Calcium sulphide is produced as a by-product in the Leblanc alkali process.

Polysulphides.—Just as with the alkali hydrosulphides, the action of excess of sulphur on hot solutions of the alkaline-

* Breteau, *Compt. rend.* (1915), **161**, 732.

earth hydrosulphides, as well as of the hydroxides, results in the formation of polysulphides of the type MS_5, and containing the anion $[S_5]^=$, which is probably $[SS_4]^=$, i.e. the sulphur analogue of the sulphate ion. It is metals of large atomic volume which form such polysulphides, and these are probably comparable with the polyhalides, e.g. CsI_5 or $Cs^+[II_4]^-$. These compounds are decomposed by acids with evolution of H_2S and precipitation of sulphur.

Chlorides

The chlorides of calcium, strontium, and barium are of the type MCl_2, and may be prepared by the methods ordinarily employed for the preparation of salts. They all form crystallohydrates; $CaCl_2$ with 6, 4, 2, and $1H_2O$, $SrCl_2$ with 6 and $2H_2O$, $BaCl_2$ with $2H_2O$ only. As with the alkali metals, power of hydration of salts diminishes with rise of atomic number from calcium to barium. When these crystallohydrates are strongly heated, in the case of strontium and barium chloride, the anhydrous salts are formed, whilst with calcium chloride partial loss of hydrochloric acid occurs as with magnesium chloride, so that the product is alkaline in reaction, and capable of absorbing carbon dioxide. This fact must be borne in mind in using fused calcium chloride for analytical purposes. The importance of this behaviour of calcium chloride in respect to the systematics of the group has already been indicated.

The solubilities of the chlorides* in water diminish from calcium to barium, and calcium chloride alone is deliquescent. Radium chloride, too, is less soluble than barium chloride.

The solubilities of the anhydrous chlorides in absolute alcohol are instructive. Calcium chloride is easily, and strontium chloride sparingly soluble, whilst barium chloride, in accordance with its more perfectly saline character, is insoluble.

* It is remarkable that calcium fluoride is insoluble. See Group VII

Calcium and strontium chlorides combine with ammonia to form the compounds $CaCl_2, 8NH_3$, and $SrCl_2, 8NH_3$; barium chloride appears to form the compound $BaCl_2, 4NH_3$.

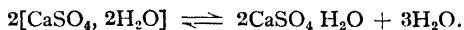
The subhalides CaF, CaCl, CaI are known.

Sulphates

The **sulphates** of **calcium, strontium,** and **barium** all crystallize in the rhombic system, being isomorphous. They show progressive insolubility in water from calcium to barium, the solubilities of the anhydrous salts in grammes per 100 c.c. at 18° being:

$CaSO_4$	$SrSO_4$	$BaSO_4$
0·2016	0·114	0·0023.

Calcium sulphate is more soluble in water at about 40° than at any other temperature, and strontium sulphate is less soluble in hot than in cold water, being precipitated from a cold solution on boiling. Precipitated barium sulphate is an extremely fine powder, but becomes distinctly crystalline and less soluble when heated or allowed to stand in contact with water. Calcium sulphate alone crystallizes with water of crystallization. Gypsum is $CaSO_4, 2H_2O$, and another hydrate, $2CaSO_4, H_2O$, exists. The manufacture and setting of plaster of Paris depend on the reversible reaction

$$2[CaSO_4, 2H_2O] \rightleftharpoons 2CaSO_4\,H_2O + 3H_2O.$$

Calcium sulphate is soluble in hot concentrated hydrochloric-acid solution, from which it crystallizes again on cooling in silky needles of $CaSO_4, 2H_2O$. The sulphates of strontium and barium are not known to form crystallohydrates; strontium sulphate is slightly soluble, and barium sulphate almost insoluble, in concentrated hydrochloric acid.

Calcium sulphate forms a double salt with potassium sulphate, $CaSO_4, K_2SO_4, H_2O$, in which a molecule of K_2SO_4 takes the place of a molecule of water in the dihydrate; and strontium sulphate also forms a compound with potassium

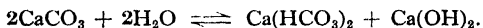
sulphate of somewhat doubtful composition, whilst barium sulphate is not known to combine with alkali sulphates. Calcium sulphate is soluble in concentrated ammonium-sulphate solution, owing to the formation of a double salt, whereas strontium and barium sulphates are insoluble. This difference is made use of as a process of analytical separation. Each of these sulphates dissolves in concentrated sulphuric acid, acid sulphates of the type $MH_2(SO_4)_2$ being formed, which are decomposed by water.

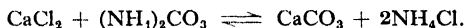
Most of the facts concerning alkaline-earth sulphates recorded in the preceding paragraphs illustrate the gradation of properties from calcium to barium, in accordance with the increase of electro-positiveness with rise of atomic number.

Other Salts

Of the other salts the **carbonates** and **phosphates** may be briefly noticed.

Calcium carbonate as aragonite, **strontium carbonate** as strontianite, and **barium carbonate** as witherite are isomorphous. The pure salts are almost but not quite insoluble in water. Pure precipitated calcium carbonate imparts an alkaline reaction to water, the very small amount dissolved suffering hydrolysis, thus:

$$2CaCO_3 + 2H_2O \rightleftharpoons Ca(HCO_3)_2 + Ca(OH)_2.$$

The reactions by which the carbonates are precipitated from the chloride solutions by ammonium carbonate are reversible, thus, e.g.:

$$CaCl_2 + (NH_4)_2CO_3 \rightleftharpoons CaCO_3 + 2NH_4Cl.$$

The precipitation is therefore rendered more complete by the use of excess of the carbonate solution; and, conversely, excess of ammonium chloride redissolves the precipitate. This reaction accounts for the incomplete precipitation of the alkaline-earth metals by ammonium carbonate, and is perceptible more especially with calcium compounds.

When calcium, strontium, or barium carbonate is suspended in water, and carbon dioxide is passed into the liquid, bicarbonate is formed in solution. These solutions, on evaporation, decompose with loss of carbon dioxide and precipitation of carbonate, though unstable solid bicarbonates of calcium and barium are said to exist.* The solution of calcium carbonate in carbonic acid accounts for the temporary hardness of water. No reliable data are available to indicate the relative stabilities or solubilities of these bicarbonates. That they are less stable than the bicarbonates of the alkalis shows that the power of a metal to form bicarbonate depends upon electro-positiveness. The converse of this is manifested in the formation of basic carbonates, as in the case of magnesium and zinc.

Of the **phosphates**, those of calcium are important. A solution of ordinary sodium phosphate, which is alkaline in reaction, precipitates normal or tribasic phosphate, $Ca_3(PO_4)_2$, from calcium-chloride solution, thus:

$$3CaCl_2 + 2Na_2HPO_4 = Ca_3(PO_4)_2 + 4NaCl + 2HCl,$$

which, on standing, is gradually converted into monohydrogen or dibasic calcium phosphate, $CaHPO_4$, thus:

$$Ca_3(PO_4)_2 + 2HCl = 2CaHPO_4 + CaCl_2.$$

This salt, which, when formed in the cold, crystallizes with 2 molecules of water, is hydrolyzed by water into $Ca_3(PO_4)_2$ and free phosphoric acid.

Normal calcium phosphate itself is hydrolyzed on prolonged treatment with water into a more basic insoluble portion, and a more acidic portion, which dissolves, giving an acid solution. In this respect calcium presents a marked contrast to the alkali metals, for normal sodium phosphate is soluble in water, and is hydrolyzed, producing an alkaline solution, owing to the powerful basigenic properties of sodium.

Normal calcium phosphate is the main constituent of bone ash. It is soluble in feeble acids, such as acetic, and even to

* E. H. Keiser and others, *J. Amer. Chem. Soc.* (1908), **30**, 1711, 1714.

some extent in carbonic acid; it is also soluble, like calcium carbonate, in certain ammonium salts.

Tetra-hydrogen or monobasic calcium phosphate, $CaH_4(PO_4)_2$, is produced by the action of sulphuric acid on $Ca_3(PO_4)_2$, thus: $Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$. The mixed product is superphosphate of lime.

The **nitrates** and **chlorates** of these metals are soluble salts.

Many salts of calcium, especially organic salts such as the acetate and butyrate, resemble the sulphate in being less soluble in hot than in cold water. They are therefore obtained crystalline by allowing their solutions to evaporate spontaneously at atmospheric temperature.

ZINC, CADMIUM, AND MERCURY

These metals are related to the metals of the calcium group in the same general manner as are copper, silver, and gold to those of the potassium group. As their positions in series may be taken to indicate, the resemblance between the sub-groups is not so well marked here as it is in the central groups. It is, however, better defined than in Group I, being shown by the preservation of the group valency of two. As already stated, magnesium forms the link between the alkaline-earth metals and the less positive metals of sub-group II B. These metals further differ from their analogues in sub-group A in forming volatile organo-metallic derivatives. With rise in atomic number the change here, as in Group I B, is from more to less electro-positive. Judged, however, by the properties of their hydroxides, zinc is less basigenic than cadmium. The relationship of mercury to cadmium is less close than that of cadmium to zinc, since the rare-earth metals intervene, and it will therefore be convenient to deal first with the chemical properties of the two former metals.

Physical Properties.—The physical properties of the metals of Group II B show regular gradation. The densities increase whilst the melting- and boiling-points decrease with

increase of atomic weight, as is shown in the appended table. In the state of vapours, the molecules are all monatomic.

	Zn	Cd	Hg
Atomic weight.. ..	65·37	112·40	200·6
Density..	7·19	8·7	13·59
* Melting-point	412°	320°	−39·4°
Boiling-point	920°	778°	360°

The metals zinc and cadmium are associated with one another as sulphides in zinc blende, which is chiefly ZnS.

In the reduction by means of carbon of the oxides, formed by roasting the sulphides, the more volatile cadmium passes over first, and is purified by redistillation.

Both metals exhibit allotropy,† and on ignition in the air burn to the monoxides; they are slowly oxidized in ordinary moist air, but do not so readily decompose water on heating as does magnesium. When immersed in water containing oxygen and carbonic acid, zinc, like lead, is slowly converted into basic carbonate. These metals are readily attacked by acids; ordinary dilute acids, except nitric acid, evolve hydrogen. Zinc is dissolved by alkalis with evolution of hydrogen. The comparison of beryllium, magnesium, and zinc with reference to their behaviour towards nitric acid and alkalis is interesting. With nitric acid there is respectively no action, evolution of gases containing hydrogen, and evolution of gases not containing hydrogen; and with alkali, there is respectively solution with evolution of hydrogen, no action, and solution with evolution of hydrogen. From these latter facts it may be concluded that the rise in basigenic properties from beryllium to magnesium is followed by a fall from magnesium to zinc. It is singular that beryllium (with aluminium) and zinc, which behave similarly with alkalis, differ entirely in their behaviour towards nitric acid.

The monoxides ZnO and CdO are basic, yielding the salts

* The exact values for melting- and boiling-points of metals cannot as a rule be stated with certainty, since different observers have recorded different values. Generally the more commonly accepted values are given.

† Cohen, *Proc. K. Akad. Wetensch. Amsterdam* (1914), **17**, 200.

of the metals on treatment with acids, and correspond with the hydroxides $Zn(OH)_2$ and $Cd(OH)_2$. These cannot, however, be prepared by the union of the oxides with water, but are obtained by precipitation of the soluble salts with alkali hydroxides. Zinc hydroxide differs from cadmium hydroxide in being soluble in caustic alkalis, just as zinc is soluble and cadmium insoluble in the same reagents; unstable zincates, which readily hydrolyze on boiling their diluted solutions, are formed in each case.* The crystallized zincates $Na[Zn(OH)_3], 3H_2O$, and $Na_2[Zn(OH)_4], 2H_2O$ are known. The conclusion that cadmium is more basigenic than zinc, although in accordance with the general rule regarding simultaneous increase of metallic properties and atomic number, is not in agreement with the positions of the elements in the electro-potential series. Both zinc and cadmium hydroxides are soluble in ammonia. This is due, not to acidic properties of the hydroxides, but to the formation of complex " ammines " of the type $[M(NH_3)_n](OH)_2$.

The peroxides ZnO_2 and CdO_2 are formed when the hydroxides are moistened with hydrogen-peroxide solution. They are thus superoxides, and are easily decomposed, giving off oxygen. The superoxides of magnesium, zinc, and cadmium, are less stable than those of the alkaline-earth metals; thus the formation of stable superoxides is a criterion of the electro-positive or basigenic properties of a metal.

Cadmous oxide and its Derivatives.—It was observed in the case of copper and gold, in Group I A, that two series of salts are known, namely, the cuprous and cupric and the aurous and auric salts; silver is remarkable for its almost constant univalency. Moreover, mercury, the last member of the sub-group now under consideration, forms two well-defined series of salts. It is of interest, therefore, to inquire whether zinc and cadmium form oxides and derivatives lower than the monoxides. Cadmium is known to form such compounds, but not zinc. When cadmic chloride is heated with

* Some at least of the zinc hydroxide is probably present in the colloidal state.

cadmium, cadmous chloride is formed; and this, on treatment with water, gives a white precipitate of cadmous hydroxide, $Cd_2(OH)_2$, which, on gentle ignition, yields cadmous oxide as a yellow powder.

The **sulphides** of zinc and cadmium are insoluble in water, and differ from the alkaline-earth sulphides in not being hydrolyzed. They are precipitated from neutral-salt solutions by hydrogen sulphide, zinc sulphide being white, and cadmium sulphide yellow. Zinc sulphide is soluble in dilute mineral acids, though not in acetic acid; in order, therefore, to secure its complete precipitation by hydrogen sulphide, ammonia or ammonium acetate must be added in excess. Cadmium sulphide, though less soluble than zinc sulphide, is dissolved by a large quantity of dilute hydrochloric or sulphuric acid.

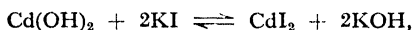
Neither of these sulphides is acidic. The fact that zinc sulphide does not dissolve in alkalis, while zinc oxide does, manifests the feebler electro-negative or non-metallic properties of sulphur as compared with oxygen.

Halides.—The halides of zinc and cadmium may be prepared by the direct union of the elements, as well as by the action of solutions of the halogen acids on the metals or their oxides or carbonates. These weak salts are solids which melt at moderately low temperatures, and may sometimes be boiled without decomposition, when they sublime in distinct crystals. They are all very soluble in water except the fluorides (cf. CaF_2), and likewise dissolve more or less readily in alcohol and ether. Zinc chloride is a white deliquescent mass, which is a powerful dehydrating agent. It crystallizes with one or three molecules of water. When its solution is evaporated, hydrochloric acid is lost, and mixtures of basic chloride $Zn(OH)Cl$ and hydroxide are formed (cf. $MgCl_2$). Zinc iodide, when exposed to the air, deliquesces and absorbs oxygen, losing iodine. The halides of cadmium, in accordance with the more basigenic character of the metal, do not undergo this kind of change.

The halides, as might be anticipated from their other properties, form numerous double salts with alkali halides. They

also combine with ammonia, forming, e.g. $ZnCl_2, 2NH_3$* and $CdCl_2, 2NH_3$, and likewise, with hydroxylamine, forming the compounds $ZnCl_2, 2NH_2OH$ and $CdCl_2, 2NH_2OH$.

A characteristic of the halides of cadmium, which is further shown in the halides and other compounds of mercury, is the small degree of their electrolytic dissociation in aqueous solution. The stability of these halides towards water is probably due partly to this cause. The above property may be illustrated in the case of cadmium iodide by adding potassium iodide solution to water in which cadmium hydroxide is suspended. The following reaction takes place:

$$Cd(OH)_2 + 2KI \rightleftharpoons CdI_2 + 2KOH,$$

and the cadmium iodide then forms the auto-complex halide $Cd[CdI_3]_2$, in which some of the cadmium is protected from the KOH so that the solution becomes alkaline.

Carbonates.—When alkali carbonates act on solutions of zinc or cadmium salts, basic carbonates of varying composition are formed. Normal zinc carbonate is known as the mineral calamine, and also is precipitated from solutions of zinc salts by potassium hydrogen carbonate, that is, when excess of HCO_3' ion is employed so as to prevent hydrolysis. Thus zinc carbonate resembles magnesium carbonate in properties, though in accordance with the less basigenic character of zinc the normal carbonate is not obtained from solution like hydrated magnesium carbonate. Cadmium carbonate is formed by adding ammonium carbonate to cadmium chloride solution.

Of the **sulphates,** that of zinc, $ZnSO_4, 7H_2O$, is isomorphous with magnesium sulphate. Its solution in water differs from that of magnesium sulphate in possessing an acid reaction due to incipient hydrolysis. A basic salt is produced by ignition, with loss of sulphur dioxide and oxygen. Cadmium sulphate departs from the form presented by magnesium and zinc sulphates, its crystals consisting of $3CdSO_4, 8H_2O$, or $CdSO_4,H_2O$;

* Probably the ammonia is associated with the cation thus: $[Zn(NH_3)_2]Cl_2$; but for a discussion of these and allied compounds, see end of Chapter XII.

$CdSO_4$, $7H_2O$ exists, however, at low temperature. Its cold aqueous solution has a neutral reaction, but becomes faintly acid when boiled. Zinc sulphate forms double salts of the type $ZnSO_4$, M_2SO_4, $6H_2O$, where $M = K$, NH_4, Rb, Cs, Tl; cadmium sulphate forms similar, isomorphous, double salts.

Zinc sulphate forms ammoniacal compounds, such as $ZnSO_4$, $2NH_3$, H_2O, whilst the anhydrous salt absorbs ammonia, yielding $ZnSO_4$, $5NH_3$. Cadmium sulphate likewise forms compounds with ammonia.

MERCURY

Mercury, like gold and thallium, forms two series of compounds: the **mercurous** corresponding with the oxide Hg_2O, and the **mercuric** corresponding with HgO. It differs in this respect from the other members of Group II, excepting cadmium, which forms the cadmous salts; but this characteristic finds many parallels in other groups. In most other cases of elements forming more than one series of compounds, the different series owe their existence to a variation in the active valency of the element. In the case of mercury, however, this is probably not the case. Mercurous chloride, when vaporized under ordinary circumstances, is completely dissociated into mercuric chloride and mercury; but when dried most carefully gives, according to Baker,* a vapour of the molecular composition Hg_2Cl_2, in which the metal is bivalent. It is probable, therefore, that the difference between mercurous and mercuric compounds is to be referred to a difference in the mass rather than the valency of the metallic radicle in the two cases. As will be seen later, mercurous in some respects resemble cuprous compounds.

Besides forming two well-defined series of compounds, mercury differs from zinc and cadmium in the ease with which its oxide HgO decomposes by heat; recalling in this respect its

* *Chem. Soc. Trans.* (1900), 77, 646.

predecessors in series, osmium, iridium, platinum, and gold. Thus mercury occurs native, and its chief natural compound, cinnabar, or mercuric sulphide, easily yields the metal on simply heating in the air,

$$HgS \rightarrow HgO \rightarrow Hg.$$

Mercury is undoubtedly less electro-positive than cadmium or zinc, as is shown by the relative position of the elements in the electro-potential series; it is also less basigenic, as judged by comparison of the general chemical properties of the three elements. Thus mercury does not displace hydrogen from dilute hydrochloric and sulphuric acids, behaving, in this respect, similarly to copper. Indeed mercury is even less electro-positive than copper, as is shown by its displacement from salt solutions by the latter metal.

Mercurous Compounds

The **oxide Hg_2O** was considered to form as a black powder when alkali hydroxides are added to mercurous salts. Analysis of various preparations by X-rays, however, has shown the presence of mercuric oxide and free mercury, hence its existence is doubtful. No mercurous hydroxide is known. In these respects, therefore, mercury differs from copper.

Mercurous sulphide, Hg_2S, has been obtained at $-10°$ C. by the action of dry hydrogen sulphide on mercurous chloride, but is decomposed at $0°$ C. to give mercury and mercuric sulphide. This mixture also results when hydrogen sulphide acts on solutions of mercurous salts.

Of the **halides, mercurous chloride,** Hg_2Cl_2 or calomel, which is volatile, is prepared by heating together mercuric chloride and mercury, or a mixture of mercuric sulphate and mercury with sodium chloride. It may be obtained in quadratic plates, and is fairly stable towards water, probably on account of its extremely small solubility. When, however, it is boiled for a long time with water, or with concentrated hydrochloric acid, some passes into solution as mercuric

chloride, while mercury is precipitated. This illustrates a tendency towards the same manner of decomposition that characterizes the oxide, and which is further illustrated by the dissociation which this compound undergoes when heated.

Mercurous bromide, Hg_2Br_2, and **iodide**, Hg_2I_2, are similar in properties to the chloride. Both may be obtained crystalline; the bromide is white and the iodide yellow. The greenish precipitate generally obtained on adding potassium-iodide solution to a mercurous salt contains finely divided mercury.* Mercurous fluoride, in contrast to the other halides, is soluble in water, and readily undergoes hydrolysis.

Mercurous sulphate, Hg_2SO_4, formed as a white crystalline powder by the action of concentrated sulphuric acid on excess of mercury, is almost insoluble in water, and is precipitated by adding sulphuric acid to a solution of mercurous nitrate. It is fairly stable towards heat, melting unchanged, but is hydrolyzed by water, with production of basic sulphate.

Mercurous nitrate, $Hg_2(NO_3)_2, H_2O$, is formed when cold, dilute nitric acid acts on mercury. Water partially hydrolyzes it.

Mercurous carbonate, Hg_2CO_3, is precipitated as a yellow powder when potassium hydrogen carbonate is added to a solution of a mercurous salt. As might be anticipated, it easily loses carbon dioxide when gently heated, and leaves a mixture of mercuric oxide and mercury. If a solution of a normal carbonate is used for the precipitation, decomposition takes place at atmospheric temperature, so unstable is mercurous carbonate. A comparison with the carbonates of zinc and cadmium further illustrates the inferior electro-positiveness of mercury.

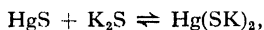
Mercuric Compounds

Mercuric oxide, HgO, is precipitated from solution of a mercuric salt, by excess of alkali hydroxide, as a yellow powder.

* This is formed by the decomposition of Hg_2I_2 in presence of excess of KI, thus: $Hg_2I_2 + 2KI = K_2HgI_4 + Hg$.
If the KI solution is dilute, the precipitate is yellow, and consists only of Hg_2I_2; if KI is added in excess, only mercury remains in the precipitate.

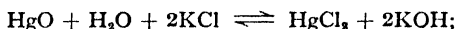
Probably the hydroxide is first formed, but is exceedingly unstable. The oxide varies in colour from yellow to red; when precipitated from hot solution it is orange, and when obtained by the ignition of the nitrate or of the metal in air, it is red and distinctly crystalline. The difference in colour probably depends on the state of subdivision, that which is most finely divided being most active chemically; the yellow variety is employed in preference to the red, for instance, in the preparation of chlorine monoxide and hypochlorous acid. The yellow form passes into the red at 400°. It is slightly soluble in water, giving an alkaline reaction, but also seems to possess very feebly acidic properties. It is decomposed into mercury and oxygen when strongly heated, first turning black. It thus closely resembles silver oxide in chemical properties.

Mercuric sulphide, HgS, which occurs naturally as cinnabar, is formed eventually as a black amorphous precipitate, when hydrogen sulphide gas is passed through a solution of a mercuric salt, unstable combinations of sulphide and other salt being first produced. Whilst mercuric oxide appears to possess no acidic properties, the sulphide is very feebly acidic. This is manifested by its solubility in concentrated alkali sulphide and polysulphide solutions, whilst it is insoluble in the corresponding hydroxides. Unstable thiosalts are produced when mercuric sulphide is dissolved, thus:

$$HgS + K_2S \rightleftharpoons Hg(SK)_2,$$

but these are decomposed by dilution and boiling. A red crystalline variety of mercuric sulphide, known as vermilion, is more stable and less soluble than the black form. On this account, and because of the solubility of the sulphide in potassium sulphide, contact with a solution of the latter gradually converts the black into the red variety. When either form is heated and the vapour quickly condensed a black sublimate is obtained, according to the rule that the less stable form is first produced. This, however, is converted into the red form by the mechanical agitation of scratching. As might be

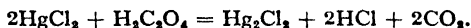
expected, cinnabar, the natural form of mercuric sulphide, consists of the more stable red kind.

Mercuric chloride, $HgCl_2$, prepared by sublimation of a mixture of mercuric sulphate and sodium chloride, crystallizes in needles, is soluble in water and very poisonous, and is known as corrosive sublimate. The aqueous solution of this salt possesses a but faintly acid reaction and shows no signs of hydrolysis. It thus differs from the mercuric oxysalts, which are freely hydrolyzed by water. The chloride does not, however, behave like the alkali and alkaline-earth chlorides, since it is soluble in alcohol and ether. Moreover, by a determination of its electric conductivity it is proved to be but slightly ionized; this may be due to the formation of an auto-complex such as $Hg[HgCl_4]$, and is the cause of its stability towards water. It is also stable towards strong sulphuric acid, like non-metallic chlorides, and is more soluble in strong hydrochloric acid than in water, owing to the formation of the compound $HHgCl_3$. It also readily forms double salts with alkali chlorides such as $KCl, HgCl_2, H_2O$, and $2KCl, HgCl_2, H_2O$. When mercuric oxide is shaken with potassium chloride solution, the liquid becomes alkaline by the following reaction:

$$HgO + H_2O + 2KCl \rightleftharpoons HgCl_2 + 2KOH;$$

the cause of which is the slight ionization of mercuric chloride, or the formation of an auto-complex. Conversely, the precipitation of mercuric oxide from the chloride solution by alkali hydroxide is never quite complete.

Various basic chlorides are known.

Mercuric chloride is easily reduced to mercurous chloride in aqueous solution, for instance, by oxalic acid:

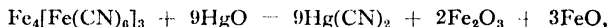
$$2HgCl_2 + H_2C_2O_4 = Hg_2Cl_2 + 2HCl + 2CO_2.$$

When stronger reducing agents, such as stannous chloride, are employed, metallic mercury is eventually produced.

The properties of **mercuric bromide** call for little remark. It is white, and sparingly soluble in water, being ionized to

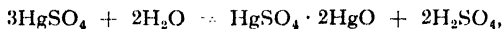
a less extent than the chloride, and more easily forming complex salts.

Mercuric iodide exists in two forms, being *enantiotropic*, like the sulphide. The red form is the more stable at ordinary temperature, but above 128° the stability of the yellow form is greater. It is very slightly soluble in water, being precipitated when potassium iodide is added to a solution of a mercuric salt. Whether produced by precipitation or sublimation the less stable yellow form first appears, but gradually changes into the more stable red form. This salt is readily soluble in alcohol. It also combines with potassium iodide, forming the compound K_2HgI_4, consisting of lemon-yellow crystals. This compound contains the stable ion HgI_4'', and exists in Nessler's solution together with potassium hydroxide, not being decomposed by this substance.

Mercuric cyanide, $Hg(CN)_2$, was obtained by Scheele by boiling water with Prussian blue and mercuric oxide, thus:

$$Fe_4[Fe(CN)_6]_3 + 9HgO = 9Hg(CN)_2 + 2Fe_2O_3 + 3FeO,$$

this reaction, like that between mercuric oxide and potassium chloride, being due to the slight ionization of the mercuric salt, which, as soon as formed, ceases to participate in the reaction. The cyanide solution is indeed practically a non-electrolyte, and is not precipitated by alkali carbonate or hydroxide solution, nor is the solid cyanide decomposed by dilute sulphuric acid; hydrogen sulphide, and the halogen acids, however, decompose the salt. The fact that mercuric cyanide is even less ionized than the halides is connected with the feebly acid nature of hydrocyanic acid itself. This salt yields mercury and cyanogen gas when heated, and forms various basic and double salts.

Mercuric sulphate and nitrate, obtained by the action of the concentrated acids on mercury, are rapidly hydrolyzed by water. The sulphate thus produces the yellow "Turpeth mineral" Hg_3SO_6,

$$3HgSO_4 + 2H_2O = HgSO_4 \cdot 2HgO + 2H_2SO_4,$$

which is sometimes considered to be the orthosulphate, that is, a derivative of $S(OH)_6$. The nitrate in contact with water gives rise to the basic salt $Hg(NO_3)_2$, 2HgO, and finally the oxide. Only basic carbonates are known, but these are not completely hydrolyzed by water.

Ammoniacal Mercuric Compounds

When ammonia is added to a solution of mercuric chloride, a white precipitate is obtained which is not mercuric hydroxide but contains nitrogen and chlorine, and has the composition $HgClNH_2$; with mercurous chloride a black powder results, but this may be shown to be a mixture of a nitrogenous mercuric compound and metallic mercury; such nitrogenous mercurous compounds probably do not exist.

Further, when precipitated mercuric oxide is suspended in dilute aqueous ammonia, a pale-yellow powder is formed, which is called Millon's base, and has the composition 2HgO, NH_3. From this compound is derived a chloride having the composition HgO, $HgClNH_2$, and a corresponding iodide HgO, $HgINH_2$, which is the substance formed in Nessler's test for ammonia.

The compound $HgClNH_2$ is called " infusible precipitate "; and when this substance is boiled with ammonium chloride solution NH_4Cl is added to the molecule, and $HgCl_2$, $2NH_3$, which is " fusible precipitate ", is formed. This compound is also produced by the action of gaseous ammonia on mercuric chloride; it is a true ammine, $[Hg(NH_3)_2]Cl_2$.

There exist also the compounds $HgCl_2$, $HgClNH_2$ and $3HgCl_2$, $2NH_3$;* as well as the nitride N_2Hg_3, which results from the action of dry ammonia on mercuric oxide at 130°, as an explosive compound, decomposed by alkalis with evolution of ammonia.

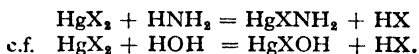
Apparently there is more than one type of mercuriammonium compound, and it is improbable that these substances can be

* Miss M. C. C. Holmes, *Chem. Soc. Trans.* (1918), **113**, 74.

represented as derivatives of the dimercuriammonium radicle (NHg_2) as was formerly supposed.* They are classified as follows: †

1. Additive compounds of mercuric salts and ammonia, i.e. mercuric ammines. Of this class " fusible precipitate ", $HgCl_2, 2NH_3$, is the best known example.

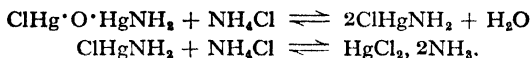
2. Ammonolyzed compounds, i.e. derivatives of mercuric salts containing the ammonia residues NH_2, NH, or N, formed by ammonolysis (analogous to hydrolysis) thus:

$$HgX_2 + HNH_2 = HgXNH_2 + HX$$
$$\text{c.f. } HgX_2 + HOH = HgXOH + HX.$$

" Infusible precipitate " (ammono-basic mercuric chloride), $HgClNH_2$, and the nitride Hg_3N_2 are examples of this class.

3. Compounds which are both hydrolyzed and ammonolyzed; e.g. Millon's base, $HO\cdot Hg\cdot O\cdot Hg\cdot NH_2$, and the corresponding chloride and iodide, $Cl\cdot Hg\cdot O\cdot Hg\cdot NH_2$ and $I\cdot Hg\cdot O\cdot Hg\cdot NH_2$. These compounds may, however, be alternatively represented thus:‡

$$HO\cdot Hg\cdot NH\cdot Hg\cdot OH; \quad Cl\cdot Hg\cdot NH\cdot Hg\cdot OH; \quad I\cdot Hg\cdot NH\cdot Hg\cdot OH.$$

The above compounds are connected together by the following reversible reactions:

$$ClHg\cdot O\cdot HgNH_2 + NH_4Cl \rightleftharpoons 2ClHgNH_2 + H_2O$$
$$ClHgNH_2 + NH_4Cl \rightleftharpoons HgCl_2, 2NH_3.$$

Although obtained in the presence of water they are related to similar compounds of other elements which are formed only when liquid ammonia is the solvent (see p. 355).

* Rammelsberg (*J. pr. Chem.*, 1888 (ii), 38, 563). Pesci (*Gazzetta*, 1889, 19, 509; 1890, 20, 485). Gaudechon (*Ann. Chim. Phys.*, 1911 (viii), 22, 145). Hofmann and Marburg (*Zeit. anorg. Chem.*, 1899, 23, 126). Franklin (*Amer. Chem. J.*, 1912 47, 361).

† Miss Holmes, *loc. cit.*

‡ Franklin, *loc. cit.*

CHAPTER VII

GROUP III

SUB-GROUP A		SUB-GROUP B
	5 B (10·9)	
	13 Al (27·1)	
21 Sc (45·1)		31 Ga (70·1)
39 Y (89·33)		49 In (114·8)
57 La (139·0)		81 Tl (204·0)

Boron and aluminium, the typical elements of this group, are more nearly related to the elements of sub-group B than to those of sub-group A. These two elements, together with gallium, indium, and thallium, will therefore be considered as constituting sub-group B.

THE RARE EARTH ELEMENTS

	At. Wt.	Rad. of ion M··· (A.U.)	Colour of ion M···
58 Cerium (Ce)	140·25	1·18	colourless
59 Praseodymium (Pr) ..	140·9	1·16	green
60 Neodymium (Nd) ..	144·3	1·15	rose
61 Illinium (Il)	——	—	——
62 Samarium (Sm) ..	150·4	1·13	yellow
63 Europium (Eu)	152·0	1·13	pale pink
64 Gadolinium (Gd) ..	157·3	1·11	colourless
65 Terbium (Tb)	159·2	1·09	colourless
66 Dysprosium (Dy) ..	162·5	1·07	yellow
67 Holmium (Ho)	163·5	1·05	yellow
68 Erbium (Er)	167·7	1·04	pink
69 Thulium (Tm)	168·5	1·04	green
70 Ytterbium (Yb)	173·5	1·00	colourless
71 Lutecium (Lu)	175·0	0.99	colourless

The elements, scandium, yttrium, and lanthanum, which are placed in sub-group A, are three of the seventeen elements commonly called the rare earth elements, the tabulation of which was for long a problem, since, in spite of their decided tervalency, they could not all be accommodated in Group III.

The conception of atomic number, and the development of Bohr's atomic structure in relation to chemical properties, has made it evident that these elements must be studied primarily in their series relationships. The three elements occupying Group III A are placed there by reason of their chemical properties and atomic numbers. Moreover, they are, each in its own period, the leading member of a series of transition elements. The remaining fourteen elements, cerium (At. No. 58) to lutecium (At. No. 71) inclusive, find their place naturally in series between lanthanum in Group III A, and hafnium, the analogue of zirconium, in Group IV B.

These seventeen elements, together with hafnium, lie between barium and tantalum on a descending portion of Lothar Meyer's atomic volume curve.

The fourteen rare earth elements depart from the typical behaviour of other transition elements in the notable constancy of their tervalency, whence it follows that the addition of electrons concomitant with increase of atomic number occurs, not in the valency group, but in some inner group where they have little effect on the chemical properties of the atom. It is believed that this addition occurs in the fourth quantum group thus:

Quantum Gp.		1	2	3	4	5	6
21 Scandium ..	..	2	8	2.6.1	2		
39 Yttrium ..	..	2	8	18	2.6.1	2	
57 Lanthanum	..	2	8	18	2.6.10	2.6.1	2
58 Cerium ..	..	2	8	18	2.6.10.1	2.6.1	2
59 Praseodymium	..	2	8	18	2.6.10.2	2.6.1	2
....	..	..	..	..	..	..	..
70 Ytterbium	..	2	8	18	2.6.10.13	2.6.1	2
71 Lutecium ..	..	2	8	18	2.6.10.14	2.6.1	2
72 Hafnium ..	..	2	8	18	2.6.10.14	2.6.2	2

It will be noted that the fourth quantum group of lanthanum contains 18 electrons, but in cerium the expansion of this group begins, to be finally completed in lutecium as a group of 32 electrons. In hafnium the building up of the fifth group begins, but until then the fifth and sixth quantum

groups remain constant. On the basis of atomic physics the rare earth elements extend from cerium to lutecium inclusive; lanthanum is excluded. The similarity of hafnium to zirconium in its chemical properties marks it as a true member of Group IV B and affords some proof of the correctness of the views here expounded. The electron structure of a rare earth element is thus:

$$2 \quad 8 \quad 18 \quad (18 + x) \; (2.6.1) \quad 2$$

where $x = 1, 2, 3, \ldots 14$ for cerium to lutecium.

In each case, the members of Group III A being included, the normal tervalent ion is attained by loss of two electrons from the outer and one from the next quantum groups, leaving, in the case of scandium, yttrium, and lanthanum, ions which show the normal periodic sub-group behaviour, but in the remainder, ions showing a marked similarity in chemical properties. The inner changes are only revealed by the production of colour and changes in the magnetic properties of the ions. The tervalency is not invariable however. Thus, cerium can utilize the new electron in the fourth group to form the ceric ion, Ce^{++++}. Similarly, but to a lesser extent—since the expansion of the fourth quantum group is now established—praseodymium shows tetravalency in PrO_2; samarium, europium and ytterbium can exhibit bivalency.

The work of von Hevesy and of Goldschmidt (1925) on the " **lanthanide contraction** " shows that the influence of these elements extends to those of higher atomic number. It is a general fact that when the valency is constant (as in a group in the periodic table), increase of atomic number produces increased atomic volume with resultant increase of electropositive character; scandium, yttrium and lanthanum form no exceptions to this rule. The rare earth elements following lanthanum, however, show progressive diminution in electropositive character, for the electrons added to the inner group neither increase the atomic volume nor completely compensate for the effect of the increased nuclear charge.

Hence these elements show diminishing atomic volumes. The same diminution can be seen in the ionic radii listed at the beginning of this chapter. Thus the ion Ho^{+++} has the same ionic radius as the ion Y^{+++} which entails similar solubilities and crystallizing powers, so they appear together in fractionations. Because of this lanthanide contraction the expected periodic increase in atomic volume of elements succeeding the rare earth elements is somewhat diminished: hence arises the remarkable chemical resemblance between the pairs of atoms or ions whose atomic or ionic radii (in Ångstrom units) are given below (Goldschmidt, 1925).

I	II	III	IV	V	VI
Ag 1·44	Cd 1·49	Sc^{+++} 0·83	Zr 1·62	Cb 1·43	Mo 1·36
(Ag^{+}1·13)	Cd^{++} 1·03	Y^{+++} 1·06			Mo^{++++} 0·68
		La^{+++} 1·22			
Au 1·44	Hg 1·49		Hf 1·66	Ta 1·42	W 1·37
(Au^{+} 1·37)	Hg^{++} 1·12	Ho^{+++} 1·05			W^{++++} 0.68

SUB-GROUP III B

Boron, Aluminium, Gallium, Indium, and Thallium

The positions of boron and aluminium in the group are, on the whole, similar to those of beryllium and magnesium in Group II. Boron is the first element in the second series in which non-metallic characteristics predominate. It is the first element to form a gaseous hydride, its oxide scarcely possesses basic properties, behaving entirely as an acidic oxide in its more stable compounds, and the properties of the element itself are those of a non-metal. Aluminium, succeeding magnesium and preceding silicon in series, presents the physical characters of a metal, and is strongly electro-positive, but acidigenic properties are indicated by its feebly acidic hydroxide, and by its chloride. From aluminium to gallium the change is of the same kind as from magnesium to zinc; thus gallium must be regarded as more acidigenic than aluminium—just as zinc is more so than magnesium—because its hydroxide is soluble

in ammonia as well as in the alkali hydroxides, aluminium hydroxide being almost insoluble in ammonia, and also because gallium alum is more easily hydrolyzed by water than aluminium alum. The heavier metals indium and thallium are more basigenic than their predecessors, as will be seen from a comparison of the properties of their oxides and halides. The tendency to form compounds of more than one type, which in the second group was observed to commence with cadmium, and to become well developed with mercury, commences in the third group with gallium, which forms a dichloride, and becomes more pronounced with indium and thallium, indium forming the chlorides InCl, $InCl_2$, and $InCl_3$, and thallium TlCl and $TlCl_3$.

Sidgwick attributes univalency here to an " inert " pair of valency electrons.

Since thallium follows mercury in series, the thallous ion may be $[Tl_2]^{++}$, but this is not certain.

The characteristics of these salts and of others related to them will be studied in the systematics of the sub-group.

The increase of atomic volume from boron (4·5) to thallium (17·3) is reflected in a general increase of electropositive character. Aluminium chloride is dimeric, $(AlCl_3)_2$, and a weak salt, but yields conducting aqueous solutions, presumably forming the complex $[Al(H_2O)_6]^{+++}$. Aluminium esters, e.g. $Al(OC_2H_5)_3$, similar to those of boron, exist. Boron and aluminium form the ions $[BF_4]^-$ and $[AlF_6]^{\equiv}$ whose structures are tetrahedral and octahedral, respectively. Both are normally tervalent, but evidently boron can attain a covalency of four, while aluminium, in the next period, can accommodate six fluorine atoms in its periphery.

Physical Properties

The Group III B elements all occur at or immediately following minima in Lothar Meyer's curve of atomic volumes, the metals being malleable and readily fusible. The physical

properties given in the table show the variation within the group.

	B	Al	Ga	In	Tl
Atomic weight	10·9	27·1	70·1	114·8	204·0
Density	2·34	2·67	5·9	7·4	11·8
Melting-point	2200°	600°	37°	155°	290°

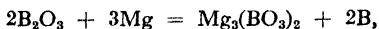
It will be seen from the table that whilst the densities of these elements gradually rise from aluminium to thallium, in the case of the melting-points there is a sudden fall from aluminium to gallium, followed by a gradual rise again to thallium. The contrast between the melting-points of aluminium and gallium clearly marks the transition from the typical elements to those of the B sub-group, a transition which is scarcely perceptible in the study of chemical properties. The rise in melting-point from gallium onwards is the opposite of what obtains in Group II B, which is exceptional; in the following sub-groups there is also rise of melting-point with rise of atomic weight. The melting-point of gallium is abnormally low, and is due to the existence of Ga_2 molecules.

BORON

Boron is obtained in an impure condition by reducing the sesquioxide, a trihalide, potassium borifluoride, or borax, with potassium, sodium, or magnesium, or by electrolysis.

The product, a brown, amorphous powder, formerly mistaken for the amorphous element,* always contains oxygen, and has been described as " boron suboxide ". It is probably a solid solution of a suboxide in boron.

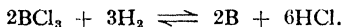
Pure boron † is obtained by the reduction of the sesquioxide with magnesium, according to the reaction:

$$2B_2O_3 + 3Mg = Mg_3(BO_3)_2 + 2B,$$

extracting the magnesium borate with acid, and heating the purified " amorphous boron " to 1200°–1700° *in vacuo*. Under

* Ray, *Chem. Soc. Trans.* (1914), **105**, 2162.
† Weintraub, *Trans. Amer. Electrochem. Soc.* (1909), **16**, 165.

these conditions magnesium boride, " boron suboxide ", and boron nitride dissociate, leaving pure fused boron.

The pure element may also be obtained by mixing the " suboxide " with excess of sodium or magnesium and heating the mixture to bright redness in hydrogen, and by the interaction of boron trichloride vapour and hydrogen at the temperature of the electric arc:

$$2BCl_3 + 3H_2 \rightleftharpoons 2B + 6HCl.$$

Pure boron is a black solid, which is not known to exhibit allotropy. It is not perceptibly oxidized when heated in air, but is slowly oxidized by concentrated nitric acid. The more active chemical properties usually attributed to boron are those of the impure amorphous product containing from 4 to 5 per cent of oxygen.

HYDRIDES

Of the elements of Series 2, boron, in accordance with its negative character, is the first to form volatile hydrides. These compounds are prepared from crude magnesium boride obtained by heating together 1 part of boron sesquioxide and 3 parts of magnesium powder. The product gives with hydrochloric acid, or better, phosphoric acid, a mixture of gases, which at liquid air temperature yields a condensate from which the hydrides, B_4H_{10}, B_5H_9, B_6H_{10} and $B_{10}H_{14}$, can be isolated by fractional distillation at low pressure.

Dihydrotetraborane, B_4H_{10}, the main product, is a colourless liquid with a disagreeable odour (B.P. 18°). It may also be prepared by the action of sodium on iododiborane, an application of the Wurtz synthesis used in carbon chemistry:

$$2B_2H_5I + 2Na = B_4H_{10} + 2NaI.$$

On heating at 90°–95°, it decomposes, yielding mainly hydrogen and **diborane,** B_2H_6, a gas (B.P. $-92{\cdot}5°$).

This hydride may also be prepared by submitting a mixture of hydrogen and BCl_3 (or BBr_3) at low pressure to a high tension discharge, producing, amongst other products, B_2H_5Cl

(or B_2H_5Br), which, on standing, decomposes giving B_2H_6 and BCl_3 (or BBr_3).

Decaborane, ($B_{10}H_{14}$), produced by heating B_2H_6 or B_4H_{10} at 115° and 90° respectively, is a volatile solid subliming in long needles which melt at 99·6° (B.P. ca. 213°). It is stable up to 170°, but decomposes rather rapidly in water at 100°.

Stock * classifies the boron hydrides thus:

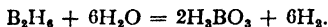
(*a*) B_nH_{n+4}.	B_2H_6 diborane	B_5H_9 penta-	B_6H_{10} hexa-	$B_{10}H_{14}$ deca-
M.P.	−165·5°	−46·6°	−65°	+99·6°

(*b*) B_nH_{n+6}.	B_4H_{10} dihydrotetraborane	B_5H_{11} dihydropentaborane	B_6H_{12}? —
M.P.	−120°	−128·5°	ca. −90°

(*c*) Several non-volatile solids not definitely characterized.

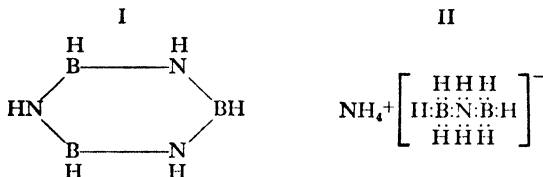
The simple hydride *borine*, BH_3, is believed to exist transiently in certain diborane reactions. Thus, diborane reacts reversibly with carbon monoxide at 100° to form *borine carbonyl*, $H_3B \leftarrow CO$ (B.P. −64°). With trimethylamine, even at −110°, diborane irreversibly forms $H_3B \leftarrow N(CH_3)_3$ (M.P. 94°). This compound is stable even at 125°.

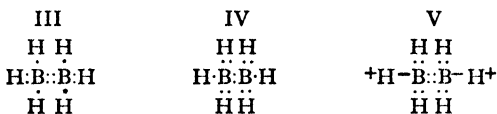
Properties.—Of the six hydrides which have been definitely characterized, B_2H_6 is a gas, $B_{10}H_{14}$ a solid, the remainder being liquids at ordinary temperature. These colourless and volatile hydrides, on standing or on heating, liberate hydrogen and form other members of the series; at a red heat they all decompose into their elements. With water they are hydrolyzed to form boric acid, B_5H_9 being the most stable in this respect:

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2.$$

With alkalis they form hypoborates (see p. 222). Halogens and halogen hydracids produce halogen-substituted products. They all combine with ammonia to form compounds such as

* Stock, *Hydrides of Boron and Silicon.*

B_2H_6, $2NH_3$; B_4H_{10}, $4NH_3$; B_5H_9, $4NH_3$; $B_{10}H_{14}$, $6NH_3$; which, from their reactions in liquid ammonia, are probably ammonium salts. When shaken with sodium or potassium amalgam, B_2H_6 and B_4H_{10} form white, solid, salt-like compounds of the type, B_2H_6, 2Na; B_4H_{10}, 2K; which are soluble in, and slowly decomposed by, water.

When B_2H_6, $2NH_3$ is heated for some time at 200° a stable colourless liquid, $B_3N_3H_6$, results (M.P. −58·0°, B.P. +53°). A fresh aqueous solution reduces permanganate, and copper salts to copper. It decomposes in water. Its properties suggest a ring structure, analogous to benzene: this has been confirmed by electron diffraction work.

Structure.—The formulæ and ready volatility of the boron hydrides suggest a similarity to the hydrocarbons, but for seven two-electron (covalent) bonds, as in C_2H_6, the simplest hydride, B_2H_6, requires 14 valency electrons, whereas its constituent atoms contribute only $2 \times 3 + 6 = 12$ valency electrons. In consequence, it was suggested that some of the hydrogen-boron linkages were one-electron (singlet) bonds, as in structures (III) and (IV), formulated by Sugden (1927) and Sidgwick (1927), respectively. An alternative structure (V), due to Wiberg (1928), avoids the necessity for singlet

III	IV	V
H H	H H	H H
H:B::B:H	H·B:B·H	+H−B::B−H+
H H	H H	H H

bonds. By acquiring an electron from a hydrogen atom each boron atom has become negatively charged and 4-covalent,

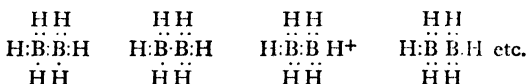
the two protons so produced being enmeshed in the electron system of the boron atoms. Thus, B_2H_6 is represented as an acid, which being double-bonded, should resemble ethylene C_2H_4, rather than ethane, C_2H_6.

The evidence summarized by Wiberg (1936) in support of (V) is inconclusive. The ultra-violet absorption spectra of B_2H_6 and C_2H_4 are similar, and their melting- and boiling-points, as well as those of their bromo- and methyl-derivatives, are closely similar. The interpretation of absorption spectra, however, is often uncertain, and melting- and boiling-points give evidence of inter- rather than of intra-molecular forces. When it reacts with sodium, diborane receives two electrons from sodium atoms to complete each boron octet, $B_2H_6 + 2Na = [H_3\bar{B}—\bar{B}H_3]2Na^+$; it thus manifests its *electronic* unsaturation, which must be expressed in any formulation and is therefore not uniquely associated with a double-bond structure. A dibasic acid of structure (V) should probably form the salt, $(NH_4)_2{}^+[H_2\bar{B} = \bar{B}H_2]$; however, Schlesinger and Burg (1938) formulate this compound as in (II), (p. 213), the same B—N—B linking occurring in its thermal decomposition product, $B_3N_3H_6$ (I). Inspection of structure (II) suggests that the salt has been formed by reactions involving the dissociation, $B_2H_6 \rightleftharpoons 2BH_3$, and the ionization of one ammonia molecule, $NH_3 \rightleftharpoons NH_2^- + H^+$. If some such route is possible, the existence of an ammonium salt affords no proof that diborane is acidic.

It is now thought that all double-bond structures must be abandoned, for Bauer (1937) has shown by electron diffraction methods that B_2H_6 possesses a tetrahedral structure similar to C_2H_6, and that it contains no double bond and no unique hydrogen atoms. For two-electron bonds, such as B—B and B—H, the interatomic distances, on modern theories, should be 1·76 and 1·18 A., respectively. The actual values, as measured by Bauer, are greater, being 1·86 and 1·27 A. This means that *all* the bonds are weaker than two-electron bonds, for they all have shared the electron deficit,

and that no double bond exists, otherwise the boron-boron distance should be less than 1·76 A.

Such a molecule cannot be represented adequately by one electronic structure using simple bond symbols, (:) or (—), for its bonds are fractional. It is rather to be represented as a " blending " of two or more reasonable, alternative structures of the conventional bond type, which are said to contribute by *resonance* * to the actual structure, whose stability is greater than that of any one component because of the energy of resonance. In diborane there are seven positions for a one-electron bond, and seven where no electron is present. This gives contributing structures, which also include (IV), such as:

```
  H H         H H          H H          H H
  ¨ ¨         ¨ ¨          ¨ ¨          ¨ ¨
H:B:B:H     H:B·B:H      H:B:B H+     H:B B.H  etc.
  · ·         · ¨          ¨ ¨          ¨ ¨
  H H         H H          H H          H H
```

Diborane is thus a *resonance hybrid*. It is not an equilibrium mixture of molecules having different structures; it is one substance having one intermediate configuration.

The zero dipole moment of diborane, its diamagnetism and its ultra-violet absorption spectrum are considered to be compatible with these views. It is probable that B_4H_{10} and B_5H_{11}, like B_2H_6, have chain structures, whilst B_5H_9, B_6H_{10} and $B_{10}H_{14}$ contain rings of four boron atoms; in each case the electron deficit requires resonating structures.

Boron alkyls, BR_3, correspond with BH_3. They are oxidized by air and water into alkyl boric acids or their esters. Boron here has a sextet of electrons and no lone pair, hence these alkyls are not basic (cf. $N(CH_3)_3$). By co-ordination the octet may be completed, thus $(CH_3)_3B$ gives $(CH_3)_3B \leftarrow NH_3$, a solid which distils unchanged.

Boron combines with carbon and with silicon at the temperature of the electric furnace, forming the **carbide** B_4C, and the

* For an authoritative discussion of " Resonance " based on quantum mechanics, see Pauling, *The Nature of the Chemical Bond.*

silicides B_3Si and B_6Si. These compounds are crystalline and very hard, and are unaffected by most chemical reagents.

Metallic **borides** likewise may be produced at very high temperatures: they are hard, inactive substances, although Mg_3B_2 and Be_3B_2 yield hydrides with acids. Calcium boride, CaB_6, unlike calcium carbide, does not react with water or dilute acids at ordinary temperature.

Halides

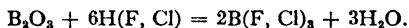
Compounds of boron with all four halogen elements are known; their physical properties are as follows:

BF_3, a colourless gas, B.P. of liquid $-101°$.
BCl_3, a colourless liquid, B.P. 12·5°.
BBr_3, a thick, colourless liquid, B.P. 90·5°.
BI_3, white, leafy crystals, M.P. 43°, B.P. 210°.

They are prepared either by the direct union of their elements, or by heating a mixture of the trioxide and charcoal with the halogen

$$B_2O_3 + 3C + 3X_2 = 2BX_3 + 3CO.$$

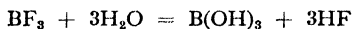
These two methods are those which are general for the preparation of non-metallic halides. In addition, the action of the dry halogen acid upon boron or its trioxide serves for the preparation of the fluoride and chloride, the former being generally obtained by treatment of the trioxide with calcium fluoride and strong sulphuric acid:

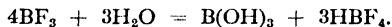
$$B_2O_3 + 6H(F, Cl) = 2B(F, Cl)_3 + 3H_2O.$$

This method is similar to that employed for the preparation of silicon tetrafluoride—not, however, the tetrachloride—but is really more characteristic of the manner of formation of metallic halides, since it is analogous to salt formation.

Its realization here is probably due to the volatility of the

fluoride and chloride, as well as to the comparative stability of these compounds towards the water which is formed in the reaction, this stability being due to the feebly non-metallic character of boron.

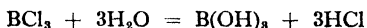
In chemical respects these halides nevertheless behave as halanhydrides, that is, they yield the oxyacid and halogen acid when acted on by water, and are not attacked by strong sulphuric acid. In the case of the fluoride, the hydrofluoric acid produced by its hydrolysis according to the reaction

$$BF_3 + 3H_2O = B(OH)_3 + 3HF$$

unites with some of the unchanged fluoride to produce hydrofluoboric acid, HBF_4, so that the complete reaction may be written

$$4BF_3 + 3H_2O = B(OH)_3 + 3HBF_4.$$

A series of salts, the fluoborates or borifluorides, is known corresponding with this acid; they are decomposed by heat, evolving the trifluoride.

Silicon tetrafluoride behaves in an analogous way with water. Thus is furnished a resemblance in chemical properties between boron and silicon; the resemblance in physical properties is also very close. The union of the fluorides of these elements with hydrofluoric acid in preference to their decomposition by water is due again to the feebly non-metallic character of the elements, and the resulting stability towards water of their fluorides. Boron trifluoride combines with ammonia, forming the compounds BF_3, NH_3; $BF_3, 2NH_3$; $BF_3, 3NH_3$.

The first action of water on boron trichloride is said to be the formation of a solid crystallohydrate, the decomposition indicated by the equation

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl$$

requiring the action of excess of water.

Boron chloride is thus less readily acted on by water than such distinctly non-metallic chlorides as PCl_3. This chloride

thus shows some approach to aluminium chloride in its behaviour towards water, though the latter is more saline, as becomes the more metallic character of aluminium.

A solid oxychloride, BOCl, is supposed to be formed when B_2O_3 and BCl_3 are heated together in a sealed tube at 150°.

OXIDES

Boron appears to form the oxides B_2O, B_2O_2, and B_4O_5 in addition to the well-known B_2O_3. These lower oxides of boron are discussed on p. 221.

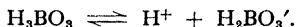
Boron trioxide, B_2O_3, is the anhydride of boric acid, from which it may be obtained by heating to redness. It is hygroscopic, passing again into boric acid by absorption of water. It resembles silica in non-volatility, in consequence of which it is able to expel the anhydrides of strong acids such as nitric and sulphuric from their salts on heating; and, as a weak acidic oxide, it forms complex salts with metallic oxides, in which the proportion of acidic oxide may be large, resembling in this respect silica and the acidic oxides of tungsten, molybdenum, and vanadium. It differs, however, from silica in its easy fusibility and power of combining with water; its salts, too, are more fusible than the analogous silicates, being formed in borax beads. Boron trioxide also enters into the composition of some silicates (e.g. tourmaline), probably playing the same rôle as its analogue aluminium trioxide, and combines with tungstic anhydride and certain metallic oxides to form complex boritungstates.

Being a feebly acidic oxide, boron trioxide also displays very feebly basic functions. For example, boric acid combines with sulphur trioxide, forming the compound $B(HSO_4)_3$, and with phosphoric and acetic acids, forming BPO_4 and $B(C_2H_3O_2)_3$ respectively. These compounds are unstable, and are easily hydrolyzed by water or dilute acids. The so-called phosphate of boron, BPO_4, is, however, insoluble in water and dilute acids, but is dissolved by alkali hydroxides, forming alkali

borate and phosphate. It is built like SiO_2, the atoms of B and P replacing Si in the net of oxygen atoms.

Boric Acid

On hydration of the trioxide, or when solutions of the borates are acidified, **orthoboric acid**, $B(OH)_3$, is formed. This acid crystallizes from water in pearly plates, is volatile in steam, and colours the Bunsen flame green. It is a very weak acid, like carbonic acid, colouring litmus solution wine red. In solution it behaves as a monobasic acid, being ionized according to the scheme:

$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3'.$$

When gently heated orthoboric acid loses water, forming first the meta- and then the pyro-acid. The transition temperature of ortho- to meta-acid is 107°–108°, and of meta- to pyro-acid 138°–140°. The orthoacid is the only one that exists permanently in solution. The relationships of these acids to one another are probably as follows:

Orthoboric acid $B(OH)_3$.
Metaboric acid (1st anhydride) $OB(OH)$.
Pyroboric acid (2nd anhydride) $4HBO_2 \rightleftharpoons H_2B_4O_7 + H_2O$.

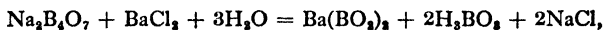
It may be pointed out that the nomenclature which is customary in the case of these acids is not consistent with that employed elsewhere, e.g. in the case of the phosphoric acids, in which the pyro- contains a larger proportion of water than the meta-acid.

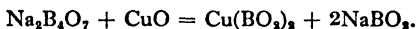
Metaboric acid is supposed to be $O = B(OH)$, and this formula is supported by cryoscopic evidence. The formula $M{\cdot}BO_2$ will therefore be used for metaborates in what follows.

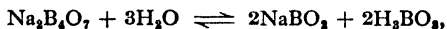
Few orthoborates are known. The magnesium salt $Mg_3(BO_3)_2$ exists, and also volatile alkyl orthoborates, such as $B(OC_2H_5)_3$, which is produced in the familiar test for a borate with alcohol and sulphuric acid. Another resemblance

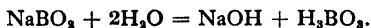
between carbonic and boric acids is shown in the fact that the only known orthocarbonates are alkyl derivatives.

The most stable salts of boric acid are the metaborates. All except those of the alkalis are insoluble in water, and are precipitated by adding a solution of borax—although a pyroborate—to a solution of the metallic salt. The following is the reaction by which barium metaborate is precipitated:

$$Na_2B_4O_7 + BaCl_2 + 3H_2O = Ba(BO_2)_2 + 2H_3BO_3 + 2NaCl,$$

whilst the borax bead reaction, in which fusible cupric metaborate is produced, may be represented thus:

$$Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2NaBO_2.$$

The best-known salt of pyroboric acid is **borax**, $Na_2B_4O_7$, $10H_2O$. An aqueous solution of this salt is alkaline in reaction on account of hydrolysis. In concentrated solution the following change probably takes place:

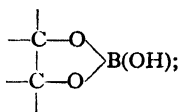
$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3,$$

which explains the precipitation of metaborates by borax solution; whilst on dilution there is an approximation to complete hydrolysis according to the following reaction:

$$NaBO_2 + 2H_2O = NaOH + H_3BO_3.$$

Thus a concentrated solution of borax added to silver nitrate solution precipitates white silver metaborate, but a dilute solution gives brown silver oxide.

Since boric acid, like carbonic acid, does not affect methyl orange, a dilute solution of borax may be titrated with standard mineral acid, by use of this indicator.

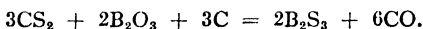
Borates still more complex than the above are known. The mineral larderellite, $(NH_4)_2B_8O_{13}$, $4H_2O$, furnishes an example.

Boric acid gives rise to remarkable compounds by combination with organic oxyacids and polyhydric alcohols. In great probability it forms with them ring compounds containing the grouping

```
   |
 —C—O\
   |   >B(OH);
 —C—O/
   |
```

and it is likely that the enormous increase in optical activity caused with compounds such as tartaric and malic acids and mannitol is attributable to this ring combination.

Such combination increases the acidic strength of boric acid; and for this reason this acid, liberated from borax by acid equivalent to the soda in the salt, can be titrated as a monobasic acid after sufficient glycerol has been added phenolphthalein being used as indicator.

Boron trisulphide, B_2S_3, is formed by passing the vapour of carbon disulphide over a heated mixture of boron trioxide and carbon:

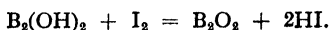
$$3CS_2 + 2B_2O_3 + 3C = 2B_2S_3 + 6CO.$$

It is a white crystalline substance, which like aluminium sulphide is hydrolyzed by water. It combines with hydrogen sulphide to form metathioboric acid, $H_2B_2S_4$, which is also decomposed by water.

Lower Compounds of Boron

When 1 part of boric anhydride is heated with $2\frac{1}{4}$ parts of magnesium, and the product is added to water, hydrogen is evolved, and a compound obtained in solution having the composition $H_6B_2O_2$.* This compound, which is called *hexahydrodioxydiboron*, appears to be an acid to which there corresponds the potassium salt $K_2[B_2H_2(OH)_2]$. Dilute sulphuric acid acts on a solution of this salt thus:

$$K_2[B_2H_2(OH)_2] + H_2SO_4 = K_2SO_4 + B_2(OH)_2 + 2H_2,$$

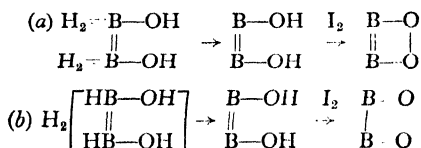
and iodine oxidizes the product thus:

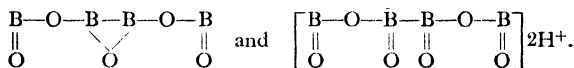
$$B_2(OH)_2 + I_2 = B_2O_2 + 2HI.$$

So the oxide $\mathbf{B_2O}$ appears to exist in combination with water, as well as $\mathbf{B_2O_2}$.

* R. C. Ray, *Chem. Soc. Trans.* (1922), **121**, 1088.

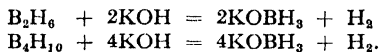
The above reactions are represented graphically by Ray in (*a*) or, following Stock, by (*b*);

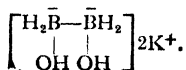
```
(a) H2 - B—OH        B—OH   I2   B—O
         ||      →   ||     →    ||  |
    H2 - B—OH        B—OH        B—O

       ┌HB—OH┐      B—OH   I2   B  O
(b) H2 │ ||  │  →   ||     →    |
       └HB—OH┘      B—OH        B  O
```

When the proportion of boric anhydride to magnesium is increased the reaction between these substances appears to take another course. Thus when 3·5 parts of boric anhydride are heated with 1 part of magnesium, and the product is extracted with water, the aqueous extract contains the compound MgB_4O_6, to which there corresponds a potassium salt $K_2B_4O_6$, and the acid $H_2B_4O_6$. The oxide $\mathbf{B_4O_5}$ and the corresponding acid $\mathbf{H_2B_4O_6}$ are believed to be constituted thus:

```
B—O—B—B—O—B             ┌B—O—B—B—O—B┐
||   \ /    ||    and   │||   || ||   ||│2H+.
O     O     O           └O    O  O    O┘
```

Hypoborates

It has been remarked above that when B_2H_6 or B_4H_{10} dissolves in alkali, hypoborate is formed. The following reactions occur:

$$B_2H_6 + 2KOH = 2KOBH_3 + H_2$$
$$B_4H_{10} + 4KOH = 4KOBH_3 + H_2.$$

The potassium salt may be obtained in octahedral crystals by carrying out the reaction at 0° and drying the product in a vacuum. It is a powerful reducing agent. Boron is believed to be 4-covalent here, and the salt is believed to have the constitution:

```
┌H2B̄—B̄H2┐
│  |   |  │2K+.
└ OH  OH ┘
```

ALUMINIUM, GALLIUM, AND INDIUM

These three metals form a group whose members are closely related, the variation in properties being in accordance with the provisions of the periodic law. *It is interesting to recall that by the* application of these provisions Mendeléeff was able to indicate the properties of his eka-aluminium, subsequently realized in the element gallium. From the analogy of the second group, gallium would be expected to be somewhat less electro-positive than aluminium, just as zinc is less electro-positive than magnesium, and this is actually the case.

Aluminium is very plentiful in nature, both as oxide and in many common silicates. Gallium and indium are widely distributed, but in minute quantities, and chiefly in zinc blendes.

Aluminium oxide is reducible only by electrolysis, or at the temperature of the electric furnace, or else by the use of sodium; but the oxides of gallium and indium are easily reduced when heated in a current of hydrogen. Aluminium is non-volatile even at a high temperature, and its salts do not colour the non-luminous gas flame, though a characteristic spectrum is revealed by the use of the electric arc or spark. Gallium compounds colour the non-luminous gas flame slightly, and the spark spectrum contains two violet lines. Indium and its compounds give a characteristic dark-blue colour to the non-luminous gas flame, which shows a well-defined spectrum. It was by means of spectrum analysis that the two latter metals were discovered.

None of these metals in the ordinary state is easily acted on by water, though aluminium in the form of amalgam, when the protection due to superficial oxidation is prevented, is gradually changed into hydroxide by contact with water, or moist air. Dilute hydrochloric and sulphuric acids dissolve all three metals; indium is readily attacked by nitric acid; dilute nitric acid slowly dissolves aluminium, and also gallium, with evolution of nitric oxide; but concentrated nitric

acid is almost without action on aluminium. Aluminium and gallium, being acidigenic, easily dissolve in alkali-hydroxide solutions, forming aluminates and gallates. Aluminium, being more acidigenic than zinc, similarly placed in Group II, is able to displace the latter from its solution in alkalis.

THE HALIDES

Halides of the group type $M^{\cdots}X_3$ are known in the case of all three metals, and in addition gallium forms a dichloride, $GaCl_2$, and indium the chlorides $InCl_2$ and InCl. Thus the tendency to form compounds of lower valency than that of the group type, which was observed in Group II B, appears again here. The trihalides are all solid substances, though volatile.

Aluminium fluoride, AlF_3, is less volatile than the other halides of this metal, and is scarcely soluble in water. It furnishes another example of the exceptional properties of fluorides (cf. AgF, CaF_2, HgF_2). It dissolves in aqueous hydrofluoric acid, forming hydrofluoaluminic acid, H_3AlF_6, the sodium salt of which occurs as the mineral cryolite.

The trichlorides all possess properties characteristic of the halides of elements of metalloidal character. Thus they are all volatile, their boiling or subliming points being approximately

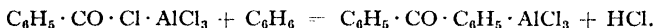
$AlCl_3$	$GaCl_3$	$InCl_3$
183°	220°	600°

Aluminium chloride shows a vapour density corresponding to Al_2Cl_6 at 200°–400°; at higher temperature it dissociates, and at 800° the vapour density corresponds to $AlCl_3$. This compound is easily soluble in alcohol and ether; it forms double compounds with ammonia and with metallic halides, for instance, $Na[Cl{\rightarrow}AlCl_3]$, which is volatile; it also combines with certain acid chlorides, such as phosphorus pentachloride and oxychloride, and with the chlorides of organic acids. This property explains the use of aluminium chloride in Friedel and Crafts' method for synthesis of ketones. In

this process the acid chloride first unites with aluminium chloride, thus:

$$C_6H_5 \cdot CO \cdot Cl + AlCl_3 = C_6H_5 \cdot CO \cdot Cl \cdot AlCl_3,$$

the product then reacting with benzene to form a crystalline compound with evolution of hydrochloric acid:

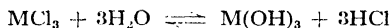
$$C_6H_5 \cdot CO \cdot Cl \cdot AlCl_3 + C_6H_6 = C_6H_5 \cdot CO \cdot C_6H_5 \cdot AlCl_3 + HCl.$$

When this compound is decomposed by water the ketone results.

This explanation does not appear to suffice for the synthesis of benzene homologues from alkyl chlorides and benzene by means of aluminium chloride.

Ferric chloride acts similarly to aluminium chloride, though less efficiently.

All the trichlorides are acted on by water, fuming in moist air. When aluminium chloride separates from solution in excess of hydrochloric acid, it forms $AlCl_3, 6H_2O$, which on heating gives the oxide and hydrochloric acid. The solutions of the chlorides in pure water easily lose hydrochloric acid on evaporation, with formation either of basic salts or the oxides.

The reaction

$$MCl_3 + 3H_2O \rightleftharpoons M(OH)_3 + 3HCl$$

is a reversible one, on account of the intermediate character of the compounds of these metals. A similar reaction is characteristic of arsenious chloride and hydroxide.

This hydrolysis is further well shown by the behaviour of the soluble basic chlorides of aluminium on dialysis, when a pure suspension* of colloidal aluminium hydroxide, the hydrosol of alumina, is formed.

Aluminium tribromide and **tri-iodide,** $AlBr_3$ and AlI_3, are similar to the trichloride; they are both volatile, and the vapour of AlI_3 is combustible. They both form crystallo-hydrates like the chloride, containing six molecules of water, which are similarly decomposed by heat.

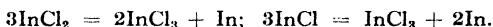
* See note, p. 226.

The iodide, like boron tri-iodide, is capable of entering into metathesis with certain chlorine compounds; e.g.

$$4AlI_3 + 3CCl_4 = 3CI_4 + 4AlCl_3.$$

Lower Chlorides of Gallium and Indium

When gallium trichloride is heated with gallium, and when indium is heated in anhydrous hydrochloric acid, the dichlorides $GaCl_2$ and $InCl_2$ are formed respectively. Indium dichloride, reacting with metallic indium, yields the volatile monochloride InCl. By the action of water both the lower chlorides of indium give the metal and the more stable trichloride:

$$3InCl_2 = 2InCl_3 + In; \quad 3InCl = InCl_3 + 2In.$$

Oxides and Hydroxides

These are of the group type $M^{\cdots}{}_2O_3$ and $M^{\cdots}(OH)_3$, together with intermediate compounds. A peroxide of aluminium, Al_2O_4, is known; and the oxide In_3O_4, formed by strong ignition of In_2O_3.

The sesquioxides, all of which are formed when the hydroxides and salts of volatile oxyacids are heated, differ from one another in some important respects.

Gallium and indium sesquioxides, in contrast with aluminium sesquioxide, are both easily reduced by carbon and hydrogen, and do not on strong ignition pass into forms insoluble in acids, as does aluminium oxide.

The hydroxides, precipitated by ammonia from their salts, are all colloids, and as such pass into colloidal suspension* in water. Aluminium hydroxide, for example, can exist in a solid form as *hydrogel*, and in colloidal suspension as *hydrosol*, this latter form being obtained by the dialysis of an aqueous solution of aluminium chloride. The hydrosol form of aluminium hydroxide is converted into the hydrogel form by the addition of ammonium chloride; presence of this reagent,

* What is commonly called a solution of a colloid is in reality a suspension. Such a " solution " does not possess the physical properties of a dilute solution.

therefore, secures the complete precipitation of aluminium hydroxide by ammonia.

Precipitation produces γ-$Al(OH)_3$, hydrargillite, which is easily soluble in dilute acids, but on standing or boiling with water forms the less soluble, γ-$AlO(OH)$, böhmite, a main constituent of bauxite. Complete dehydration produces γ-Al_2O_3. A parallel, more compact and stable α-series exists: thus α-$AlO(OH)$ is diaspore, α-Al_2O_3 is corundum. Ferric oxide and its hydroxides yield two similar series.

The hydroxides of aluminium, gallium, and indium possess, in addition to their feebly basic, feebly acidic properties. Thus, whilst they all yield solutions of their salts with excess of acid, they are all soluble in alkali hydroxides; gallium hydroxide is also soluble in ammonia, from which it appears to be more acidic than its congeners, a conclusion which is confirmed by the more ready hydrolysis of gallium salts. Of the alkali salts thus produced, the aluminates are best known.

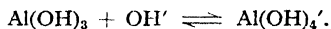
The question has been discussed * whether a solution of aluminium hydroxide in alkali contains chiefly or only aluminate, or whether the alkali remains for the most part uncombined, and serves only to retain the alumina in the state of colloidal hydrosol. It has been found from a study of variation of hydroxidion concentration when sodium or potassium hydroxide is added to aluminium chloride solution, that three times as much alkali is needed to precipitate completely the hydroxide as is subsequently required to dissolve it. This points to the following reactions taking place:

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NaCl$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O;$$

so that $Al(OH)_3$ does not remain in the free hydrosol condition. Moreover, a number of solid aluminates have been obtained, the alkali salts conforming to the type $M{\cdot}AlO_2$. $MgAl_2O_4$ occurs as the mineral spinelle.

* Hildebrand, *J. Amer. Chem. Soc.* (1913), **35**, 864. Blum, *J. Amer. Chem. Soc.* (1913), **35**, 1499; (1914), **36**, 2383.

According to another view* aluminates are additive compounds, e.g. NaOH, $Al(OH)_3$, or rather salts of aquoaluminic acid $H[Al(OH)_4]$, the formation of the aluminic acid ion being thus represented:

$$Al(OH)_3 + OH' \rightleftharpoons Al(OH)_4'.$$

Solutions of alkali tartrates, citrates, and malates prevent the precipitation of aluminium hydroxide by alkali hydroxide. This phenomenon, which is analogous to that presented by cupric and iron salts, is due to the formation of complex acidic ions. When alumina is fused in the oxy-hydrogen flame with small quantities of chromic oxide, and with a mixture of ferrosoferric oxide and titanium oxide, artificial ruby and sapphire are produced respectively.

Aluminium hydroxide combines with various organic dyestuffs, forming " lakes ".

Sulphates

The sulphates of these three metals of the type $M^{\cdots}{}_2(SO_4)_3$ are formed by the action of excess of sulphuric acid on the oxides or hydroxides; they are all very soluble in water, and suffer hydrolysis, easily giving rise to basic salts.

Aluminium sulphate, $Al_2(SO_4)_3$, $18H_2O$, crystallizes in lustrous scales. Its aqueous solution reacts acid, and dissolves magnesium with evolution of hydrogen; various basic sulphates have been described, e.g. $Al_2O(SO_4)_2$.

Alums, possessing the general formula $M^{\cdot}{}_2SO_4$, $R^{\cdots}{}_2(SO_4)_3$, $24H_2O$, are formed by the sulphates of these metals, and are less soluble in water than the single salts. They are isomorphous, crystallizing in regular octahedra; similarly constituted alums are also formed by ferric, chromic, and manganic and other sulphates, and also by analogous selenates. The stability of these double sulphates, as well as their insolubility in water, increases with increase of electro-potential difference

* Pfeiffer. *Ber.* (1907), **40**, 4036. Heyrovsky, *Chem. Soc. Trans.* (1920), **117**, 1013.

between the metals, as was pointed out in Chapter V, page 162. When dissolved in water, alums break up more or less into mixtures of the single salts. Alkali, added to alum solution till a precipitate is about to be formed, produces " neutral alum " from which, on heating, the basic double salt K_2SO_4, $Al_2(SO_4)_3$, $4Al(OH)_3$ separates. Of pseudo-alums of the type $M^{\cdot\cdot}SO_4$, $Al_2(SO_4)_3$, $24H_2O$, the ferrous salt is well known. The salt $MnSO_4$, $Al_2(SO_4)_3$, $22H_2O$ also exists.

Other Salts

Of the other salts, the **nitrates** are soluble in water, that of aluminium being decomposed at 150°, leaving the oxide. **Aluminium Phosphate**, $AlPO_4$, is easily soluble in dilute hydrochloric, and sparingly soluble in dilute acetic acid. On boiling the latter solution a basic salt is precipitated.

None of these metals yields a carbonate; alkali carbonates precipitate the hydroxides. Similarly, the sulphides are not formed in the wet way, hydroxides resulting when alkali sulphides act on the salt solutions. **Indium sulphide**, In_2S_3, however, is formed as a yellow precipitate when hydrogen sulphide is passed through a neutral indium-salt solution.

THALLIUM

Thallium, the element of highest atomic weight of the group, occurs associated with varieties of pyrites in zinc ores, with potassium in carnallite and sylvine, and with silver and copper in the mineral Crookesite. Like gallium and indium it owes its discovery to spectrum analysis, and like them it is easily reducible from its oxides or salts, being usually precipitated from a solution of its sulphate by zinc.

In physical properties thallium closely resembles its successor in series, lead. It has a bluish, lead-like tint, is soft and malleable but not tenacious, and marks paper. It has a density of 11·85, exists in two enantiotropic forms with a transition temperature of 226°, melts at 302°, and is volatile in a

stream of hydrogen; lead with a density of 11·34 melts at 326° and is also somewhat volatile. Thallium colours the non-luminous gas flame bright green, its spectrum consisting of a single green line. In this respect it resembles the alkali metals.

The mode of natural occurrence of thallium, together with such varied elements as zinc, potassium, and silver or copper, as well as its physical properties and the position assigned to it in the periodic classification, make the discussion of the chemical properties and analogies of this element a matter of more than usual interest.

Gold and mercury, occupying positions in Groups I and II analogous to that occupied by thallium in Group III, present two series of compounds: the aurous and auric, and the mercurous and mercuric compounds respectively. Thallium likewise forms thallous and thallic compounds of the same types as the aurous and auric derivatives. Now whilst gold, and to some extent mercury, show the feeble reactivity which is specially characteristic of the eighth group, so that their compounds, especially those of lower valency, are somewhat unstable, the thallous compounds exhibit no such property. These compounds, therefore, are not very similar to the aurous compounds, but resemble instead the compounds of the alkali metals in Group I A, being ionized to about the same extent in aqueous solution. This resemblance, however, although important, does not exhaust the analogies of thallous compounds.

The neighbours of thallium in Groups II and IV are mercury and lead respectively, and it has already been seen that metallic thallium resembles lead. Thallous salts also resemble mercurous and silver, and especially lead salts. Thallic salts, although typical of the third group, of which thallium is a member, are rather unstable; they somewhat resemble auric compounds.

All these relationships will be made plain in the study of the compounds of thallium which follows, this metal afford-

ing one of the most remarkable illustrations of the variation of chemical character with variation of valency.

Thallous Compounds

Thallium gradually oxidizes in moist air, forming, when carbon dioxide is absent, the hydroxide TlOH, and when it is present forming the carbonate Tl_2CO_3. On account of this oxidation, the grey mark made by the metal on paper gradually disappears on exposure to air.

Thallous hydroxide crystallizes from a strong solution, which may be prepared by acting on a solution of the sulphate with the requisite amount of barium hydroxide, in yellow crystals, TlOH, H_2O, which lose all their water at 100°, leaving thallous oxide, Tl_2O, as a brown powder. The hydroxide is regenerated from the oxide by means of water; its solution in water is strongly alkaline, and absorbs carbon dioxide from the air. In these respects thallous hydroxide resembles the alkali hydroxides; it is, however, less stable than these, as the effect of heating it shows.

Thallous sulphide, Tl_2S, differs from the alkali sulphides in being insoluble in water; it is formed as a black precipitate on passing hydrogen sulphide into a neutral solution of thallous sulphate, but the precipitation is incomplete since the sulphide, like zinc sulphide, is soluble in dilute mineral acids. It is insoluble in alkali-sulphide solutions.

Halides.—Thallous fluoride, unlike the other halides, is easily soluble in water, thus resembling silver fluoride, and furnishing another example of the exceptional properties of fluorides. Like potassium fluoride, it readily forms a double fluoride, $TlHF_2$.

The chloride, bromide, and iodide are all formed by precipitation, and stand in order of decreasing solubility. About 2·4 parts of the chloride dissolve in 100 parts of boiling water. The chloride is also the product of combustion of thallium in chlorine; like mercurous chloride it is volatile (above 700°),

but the vapour shows the normal density. Thallous chloride is white, and isomorphous with the alkali chlorides, but turns violet on exposure to light, like silver chloride; the bromide is pale yellow and the iodide bright yellow like lead iodide. Thus the halides are closely related to those of Group I B, and also show some analogies with mercurous and lead halides.

Thallous sulphate, Tl_2SO_4, closely resembles the alkali sulphates. It is soluble in water and isomorphous with potassium sulphate, and forms an acid sulphate $TlHSO_4$. The most striking analogy, however, is shown in the existence of double salts, such as Tl_2SO_4, $MgSO_4$, $6H_2O$, isomorphous with K_2SO_4, $MgSO_4$, $6H_2O$, and the alums Tl_2SO_4 $(Al_2Fe_2Cr_2)$ $(SO_4)_3$, $24H_2O$, which are isomorphous with potassium alum.

It has been shown by Tutton* that thallium lies near to rubidium and ammonium, between potassium and cæsium, in the isomorphous series of the alkali salts, but that the optical properties of thallous salts do not support this relationship.

Thallous carbonate, Tl_2CO_3, is sparingly soluble in water, from which it crystallizes anhydrous; it is more soluble in water containing carbonic acid than in pure water, bicarbonate being formed. In properties thallous carbonate lies between the carbonates of lithium and sodium. The thallous phosphates also show similar relationships as regards solubility, and they are isomorphous with the corresponding potassium compounds; Tl_3PO_4 is sparingly soluble, Tl_2HPO_4, H_2O and TlH_2PO_4 are readily soluble in water.

The chlorate $TlClO_3$ is sparingly soluble in water; the perchlorate $TlClO_4$ and nitrate $TlNO_3$ are isomorphous with the corresponding potassium salts. The chromate Tl_2CrO_4 is an insoluble yellow powder resembling lead chromate. Hydrochloroplatinic acid, H_2PtCl_6, precipitates the platinichloride Tl_2PtCl_6 from solutions of thallous salts.

* *Proc. Roy. Soc.*, 79, A, 351.

THALLIC COMPOUNDS

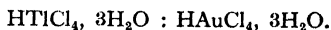
Thallic oxide, Tl_2O_3, although the typical oxide of thallium, is less stable than thallous oxide. It is formed by the combustion of the metal in oxygen, and by the oxidation of thallous oxide by bromine; it is also produced at the anode in the electrolysis of thallous salts. It is a black powder insoluble in water and alkalis, which when heated fuses at 720° and decomposes above 800° into thallous oxide and oxygen. It dissolves to some extent in dilute hydrochloric and sulphuric acids, forming thallic salts, but chlorine and oxygen are readily evolved on warming, especially with the more concentrated acids, thallous salts being formed in solution. In all these respects thallic oxide resembles the group-type oxides, PbO_2 and Bi_2O_5, and thus behaves more as a basic peroxide than a true basic oxide. It differs, however, from the two latter oxides in possessing no acidic properties.

Thallic hydroxide is formed as a brown precipitate when alkalis are added to solutions of thallic salts, or by the hydrolysis of these salts by much water; it is also produced by the oxidation of thallous salts by alkali hypochlorites, and on drying has the composition TlOOH or Tl_2O_3, H_2O. Unlike the other hydroxides of the sub-group, it possesses no acidic properties, being insoluble in alkalis. It is a very weak base, and the thallic salts corresponding to it are generally decomposed by water. The superior acidic properties possessed by aluminium over thallic hydroxide are in accord with the principles of the periodic law; that thallium is at the same time less electro-positive than aluminium, as shown by the relative positions of the two metals in the electro-potential series, shows how widely different the relationships of elements with regard to these two classes of properties may be.

Thallic chloride, $TlCl_3$, is the most stable thallic salt. It is formed by the action of chlorine on thallous chloride, and when anhydrous is a crystalline mass melting at 24°.* It is

* R. J. Meyer, *Zeit. anorg. Chem.* (1900), **24**, 321.

soluble in organic solvents and forms compounds with alcohol and ether, as well as crystallizing with water in the forms $TlCl_3, H_2O$ and $TlCl_3, 4H_2O$. It likewise forms with hydrochloric acid the crystalline compound $TlCl_3 \cdot HCl, 3H_2O$, which is analogous to chlorauric acid, thus:

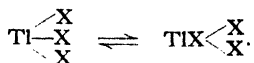
$$HTlCl_4, 3H_2O : HAuCl_4, 3H_2O.$$

Unlike the latter substance, however, chlorothallic acid of the above type does not form alkali salts, for when a solution of this substance is neutralized with potassium hydroxide the following reaction takes place:

$$2HTlCl_4 + 2KOH = TlCl_3 \cdot 2KCl + TlCl_3 + 2H_2O.$$

Probably, therefore, the compound $HTlCl_4, 3H_2O$, which exists in the solid state, is broken up in solution.

In addition to forming double chlorides with the alkali metals, thallic chloride also combines with thallous chloride. Thus when thallium is carefully warmed in chlorine the compound $TlCl \cdot TlCl_3$ or $TlTlCl_4$ is formed; this on stronger heating gives $3TlCl \cdot TlCl_3$, by which reaction the relative instability of the higher type is shown.

From a nitric-acid solution of thallic chloride the chlorine is not completely precipitated by silver nitrate. This is due to ionization not proceeding to all the chlorine atoms within the molecule, as in the case of green chromic chloride (q.v.). The isomorphism of thallic iodide with rubidium and cæsium tri-iodides suggests that thallic halides may possess the constitution $TlX\langle^{X}_{X}$. The instability of the thallic as compared with the thallous type, as well as the resemblance between thallous and alkali salts, make credible the possibility of a transformation such as the following:

$$Tl \begin{cases} X \\ X \\ X \end{cases} \rightleftharpoons TlX\langle^{X}_{X}.$$

Thallic sulphate, $Tl_2(SO_4)_3$, differs from the allied sul-

phates of the sub-group in forming an ammonium alum only A double sulphate, Tl_2SO_4, $Tl_2(SO_4)_3$, is known, as well as compounds of the type M_2SO_4, $Tl_2(SO_4)_3$, $8H_2O$, with which double sulphates containing aluminium, indium, and rare earth metals correspond.

SUB-GROUP III A

Scandium, Yttrium, Lanthanum: the Rare-earth Metals

Scandium, yttrium, and lanthanum occupy definite positions in the periodic table, and are undoubtedly members of Group III A. Chemically speaking, however, they are not to be separated from the companion metals of the rare earths, which follow lanthanum.

OCCURRENCE AND SEPARATION

These substances are encountered in exceedingly rare minerals in the form of silicates such as *gadolinite* (YCePrNdLa), *cerite* (CePrNdLa), or columbates, tantalates, phosphates, fluorides, and uranates, such as *samarskite*, which contains Ta_2O_5, Nb_2O_5, UO_3 and Ce, Pr, Nd, La, and Y.

Owing to the scarcity of the minerals containing these rare earths, and the close similarity between the oxides and salts of the elements they contain, the difficulty of effecting a complete separation of these elements is very great.

The processes available are those of fractionation; for instance, advantage is taken of the variation in decomposition temperature of the nitrates, or fractional precipitation of the hydroxides by alkalis is resorted to, when the less basic earths separate first in the order Lu to La; fractional crystallization of salts such as formates, oxalates, or double sulphates and nitrates is also an effective means of separation. The course of the separation may be followed by estimations of the equivalents of the oxides, by the study of their absorption or emission spectra, or by their X-ray spectra.

The difficulty of separating these elements from their naturally occurring mixtures, and the fact that processes of

fractional precipitation yielded in the case of yttria products which showed different phosphorescent spectra, led Crookes in 1886 to formulate his theory that these " elements " were themselves complex but contained simpler components called " meta-elements ". This view was opposed to Lecoq de Boisbaudran, who concluded that the yttria phosphorescence was due to impurity; and Urbain and his collaborators have confirmed the latter view. Moreover, according to the idea of atomic numbers, all the rare-earth metals are now known.

Nevertheless, fractional methods of separation have contributed greatly to our knowledge of these metals, and have been the chief means of separating them one from another. The case of *didymium* furnishes an interesting example. This name was originally given to a supposed element discovered by Mosander in 1841, on account of the close relationship of its compounds to those of lanthanum, from which it was separated by this chemist. From didymia, its oxide, a new earth, *samaria*, was isolated by Lecoq de Boisbaudran in 1879; and the residue, which for a time was considered to be the oxide of a single metal, didymium, with an atomic weight equal to about 140, was resolved into two constituents by Auer von Welsbach in 1885. The purified didymium salts are red or violet, and give a characteristic absorption spectrum when in solution. The oxide is of a dingy blue colour. By fractional crystallization of a nitric acid solution of a double nitrate of the metal and ammonium, von Welsbach obtained two salts which were bright green and amethyst coloured respectively, and whose oxides were respectively greenish white and pale blue. The absorption spectra of these salts are distinct from one another, but when their solutions are mixed in suitable proportions the original didymium spectrum is reproduced. Thus the original didymium was separated into two elements which were named *praseodymium* (Pr) and *neodymium* (Nd) respectively, their atomic weights being Pr, 140·9 and Nd, 144·3.

Element No. 61, predicted on the basis of atomic number, was discovered in 1926 by Hopkins and his co-workers and

named *illinium* (Il). It was discovered almost simultaneously by Rolla in Italy. Crystallization of rare earths as double magnesium nitrates gave purified samples showing X-ray lines corresponding to an element of atomic number 61.

CLASSIFICATION

Analytically the rare earth metals resemble aluminium and chromium, but they also show a likeness to the alkaline earth metals, e.g. in forming solid hydrides, and also to bismuth in forming the oxychlorides MOCl.

These metals are now divided into three groups, according to differences in the properties of their compounds. These groups are: Cerium Group—La, Ce, Pr, Nd, Sm; Terbium Group—Eu, Gd, Tb; Yttrium Group—Dy, Ho, Y, Er, Tm, Yb, Lu; and some of their chief differences are:

(i) Nitrates of the metals of the cerium and terbium groups form characteristic double salts with the nitrates of uni- and bivalent metals; but nitrates of the yttrium group do not.

(ii) Double sulphates of the cerium group metals and potassium are insoluble in cold saturated potassium sulphate solution; similar salts of the terbium group metals are sparingly soluble, and those of the yttrium group metals readily soluble in the same solution.

(iii) Platinocyanides of the metals of the cerium and terbium groups resemble one another, but differ from those of the yttrium group metals.

COMPOUNDS OF THE RARE EARTH ELEMENTS

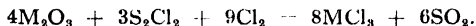
The metals, obtained by electrolysis of fused fluorides or chlorides, or by the aluminothermic process, are lustrous and fairly stable in air, but are difficult to obtain pure. The densities and melting points of a few are given below:

	Y	La	Ce	Pr	Nd	Sm
Dens.	4·57	6·15	6·78	6·60	7·05	7·75
M.P.	1475°	810°	623°	940°	840°	—

The typical **oxides**, M_2O_3—the rare earths themselves—are obtained by heating the nitrates, hydroxides, sulphates, or oxalates; the amorphous products are soluble in acids. A few higher oxides are known, CeO_2, PrO_2, Pr_4O_7, and Tb_4O_7, whilst alkaline hydrogen peroxide forms peroxyhydroxides, $M(OH)_3OOH$, where M = La, Ce (and also Ti, Zr and Hf).

The gelatinous **hydroxides,** $M(OH)_3$, are insoluble in alkali, being more basic than aluminium hydroxide: indeed lanthanum hydroxide is sufficiently basic to absorb carbon dioxide from the air.

The anhydrous **chlorides,** MCl_3 can be prepared by passing chlorine mixed with sulphur chloride vapour over the heated oxide: a method of general application.

$$4M_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8MCl_3 + 6SO_2.$$

A mixture of the oxide and sulphur, when treated similarly with bromine, yields the corresponding bromide. The chlorides are non-volatile at red heat and are hygroscopic, dissolving in water with heat evolution. They are also soluble in alcohol.

The sulphides, M_2S_3, like Al_2S_3, are decomposed by water. The nitrates are soluble crystalline salts giving double nitrates of the type $2M^{\cdot}NO_3$, $R^{\cdot\cdot}(NO_3)_3$. The sulphates are sparingly soluble and form no alums. The carbonates, fluorides and phosphates are practically insoluble in water.

In general, the salts of these metals have properties corresponding to moderately strong bases.

The order of decreasing basic strength, as determined by the readiness of decomposition of the nitrates by heat, and the relative degrees of hydrolysis of aqueous solutions of the sulphates, is: La, Ce^{III}, Pr, Nd and Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, (Sc), (Ce^{IV}). This order also corresponds with that of the precipitation of the hydroxides from mixed salt solution by the gradual addition of alkali, and, with the exception of yttrium and scandium, also accords with the atomic-weight sequence. The rare-earth metals, and particu-

larly cerium, find useful application in various ways. Metallic cerium is the essential constituent of pyrophoric alloys; ceria (CeO_2) forms 1 per cent of the incandescent gas mantle; cerium glass has the power of absorbing ultra-violet and heat rays; cerium salts have a limited use in photography and medicine.

Cerium Compounds

Cerium occurs as the phosphate associated with thoria in monazite sand.

Besides forming compounds in which it is tervalent, cerium is also quadrivalent and so related to thorium in Group IV.

Cerous compounds. The oxide, Ce_2O_3, is not formed when oxy-salts are decomposed by heat but is obtained from the dioxide, CeO_2, by reduction with calcium. It readily oxidizes again. Similarly the hydroxide, $Ce(OH)_3$ rapidly oxidizes in air to yellow ceric hydroxide.

The stable chloride, $CeCl_3$ is white, crystalline, and soluble in water. It gives hydrates.

The sulphate, $Ce_2(SO_4)_3$ gives hydrates and double salts. The nitrate $Ce(NO_3)_3$, $6H_2O$, and the insoluble carbonate both form double salts.

Ceric Compounds.—Ceric oxide, or ceria, CeO_2, is produced when oxy-salts of cerium are decomposed by heat. When pure it is white or faintly yellow. It may be obtained hydrated and colloidal (cf. ThO_2).

Ceric sulphate, $Ce(SO_4)_2$, $4H_2O$ forms soluble deep yellow crystals, and yields double salts. This substance may, with advantage, replace permanganate as an oxidant in volumetric analyses, since the change $Ce^{IV} \rightarrow Ce^{III}$ is simpler than the permanganate change, $MnO_4^- \rightarrow Mn^{++}$.

The chloride, $CeCl_4$, is unstable, readily reducing to $CeCl_3$, but the fluoride is a stable solid.

The simple nitrate is unknown, but various double nitrates exist, e.g. $Ce(NO_3)_4$, $2NH_4NO_3$, an orange-yellow substance used in the preparation of ceria.

CHAPTER VIII

GROUP IV

Sub-group A			Sub-group B
		6 C (12·00)	
		14 Si (28·3)	
22 Ti	(48·1)		32 Ge (72·5)
40 Zr	(90·6)		50 Sn (119·0)
72 Hf	(178·6)		82 Pb (207·20)
90 Th	(232·4)		

Group IV may be regarded as the transition group, linking the more positive elements of Groups I to III with the more negative elements of Groups V to VII. As in most other groups, there is a rise in metallic characters with rise of atomic number in both sub-groups, the members of the A sub-group being more metallic than those of the B sub-group.

This intermediate character is strongly developed in the first typical element, carbon, which is a unique member of the tetrad, boron, carbon, silicon and nitrogen. Possessing four valency electrons and a small atomic volume, its compounds are predominantly covalent. The completed carbon octet is not readily attacked by reagents. Hydride formation, foreshadowed by boron, reaches a maximum in the neutral hydrocarbons, and continues to a limited degree in the hydrides of nitrogen, two of which are basic. The hydrides of boron and silicon are reactive towards oxygen, those of carbon and nitrogen are relatively stable. These general tendencies are further illustrated by the natural occurrence of boron and silicon as oxygen compounds only, whilst carbon exists free, in hydrocarbons, and in carbonates.

As regards the sub-groups A and B, it should be observed that, in their respective periods, the A members are four places behind and the B members four places before an inert gas, a symmetrical placing which endows corresponding ele-

ments with somewhat similar atomic volumes, and results in a closer similarity than is found in any other group.

The electronic arrangements of elements in the A and B sub-groups are exemplified by titanium and germanium respectively, thus:

A.	Ti	2 | 8 | 8.2 | 2
B.	Ge	2 | 8 | 18 | 4.

Since the A members are transition elements, the penultimate quantum group does not remain inviolate, and valencies of 2, 3 and 4, are shown by titanium and zirconium; thorium shows quadrivalency only. In the B elements, the group valency of four is possible without encroachment on the previous quantum group of 18 electrons and the polyvalency exhibited in, e.g. $SnCl_4$ and $SnCl_2$, $PbCl_4$ and $PbCl_2$, is of another type, possibly due, as Sidgwick suggests, to one pair of the electrons becoming inert.

On electronic principles, IV B elements in their reactions should advance to an inert gas configuration by acquiring four electrons in covalent linking, whilst IV A elements should tend to revert to the previous inert gas by losing four electrons to form the ion M^{++++}, and give electrovalent linking. Highly charged ions such as M^{++++}, or even M^{++}, will only exist if the atomic volume be sufficiently large (Fajans' rules), and in both sub-groups the low atomic volumes favour covalency, the A elements in such a case gaining electrons. Nevertheless, because of the more electropositive character of the A sub-group elements, metallic properties appear earlier than in the B sub-group. Thus, while $TiCl_4$ is a halanhydride, $ThCl_4$ is a stable salt; $PbCl_4$ is covalent and unstable, but Pb^{++} forms salts.

The members of the B sub-group, together with carbon and silicon, which may appropriately be considered to belong to this sub-group, alone form volatile hydrides and volatile organo-metallic compounds.

The more salient common characteristics of the group are:

the display of the maximum valency of four in the hydrides MH_4 and the halides MX_4; the formation of typical oxides MO_2, generally of acidic character; also the combination of the tetrahalides with the corresponding halogen acids and alkali salts to form complex acids and salts, chief among these being the isomorphous complex fluorides of the type R_2MF_6.

Excepting CO_2 and dimorphous ThO_2 all the crystalline dioxides are trimorphous. The three forms of TiO_2 have corresponding isomorphs in the SnO_2 structures, and one form of GeO_2 is isomorphous with quartz and another with *cassiterite* (SnO_2) and *plattnerite* (PbO_2). With the exception of carbon and perhaps hafnium, they all form heteropolyacids (q.v.). Tetra-hydrated pergermanates, $K_2Ge_2O_7$ and Na_2GeO_5, and an unstable perstannate, $Na_2Sn_2O_7$, $3H_2O$, are analogous to the per-compounds of the IV A elements. True persilicates are doubtful.

SUB-GROUP IV B

Carbon, Silicon, Germanium, Tin, and Lead

The non-metallic elements, carbon and silicon, are linked by germanium with the more metallic elements tin and lead, just as in Group V B nitrogen and phosphorus are linked by arsenic with antimony and bismuth. The modes of occurrence and extraction of carbon are in many respects exceptional, but the occurrence of silicon in silicates, and its preparation by the reduction of silicifluorides with potassium or aluminium, are characteristic of non-metallic elements, whilst the occurrence and manner of extraction of tin and lead are characteristic rather of metals. Carbon and silicon, moreover, possess low atomic volumes and high melting-points, and in the amorphous state are bad conductors of heat and electricity; these are characteristics of non-metals, which are not shown by the higher members of the sub-group. Carbon and silicon display well-defined allotropy; tin also occurs in three different forms, and several allotropic forms of lead appear to exist.

Some physical properties of these elements are here shown:

	C	Si	Ge	Sn	Pb
Density . .	1·76 amorphous 2·06 graphite 3·5 diamond	2·35 amorphous	5·47	7·3 tetragonal 6·5 rhombic 5·3 grey	11·34
Melting-point	3600°	1410°	958°	231·8°	327°
Boiling-point	?	2600°	2700°	2260°	1620°

It is to be observed that there is a rise in density on passing from non-metallic carbon to metallic lead, and a fall in melting-point. A comparison of physical properties shows that **carbon** and **silicon** resemble one another in the nature of their allotropic forms. Amorphous silicon is a brown powder which, like amorphous carbon, burns in the air, producing the dioxide, and unites with fluorine at ordinary temperature, forming the tetrafluoride. Silicon unites with chlorine at 450°, and with bromine at 500°, though not directly with iodine; carbon, however, unites directly neither with chlorine, bromine, nor iodine. Carbon and silicon combine together at the temperature of the electric furnace, forming silicon carbide,* SiC, a very hard substance used as an abrasive. Two other forms of silicon besides the amorphous variety have been described, being known as graphitic and adamantine silicon. The two forms are probably identical with one another, both being obtained by the reduction of silica or a silicifluoride in presence of molten aluminium, from which the silicon crystallizes in black, shining, regular octahedra, isomorphous with diamond. Carbon, however, occurs in two distinctly crystalline forms, graphite and diamond. Graphite is formed when carbon crystallizes from molten iron under atmospheric pressure, diamond being formed by crystallization from the same solvent by sudden cooling under high pressure. That a difference of pressure chiefly determines which allotropic form is produced is shown by the fact that when diamond is heated to a high tem-

* This substance is widely known by the trade-name " carborundum ".

perature under ordinary pressure it is converted into graphite.

Although in the free state carbon resembles silicon, in its compounds its relationship to this and the remaining elements of the group is not so well marked. It is distinguished by the number and stability of its hydrides—the hydrocarbons—the formation of which depends upon the power possessed by carbon atoms of uniting with one another in chains and rings, a phenomenon to which some analogy is presented by silicon, for instance in the compound Si_6Cl_{14}, which probably contains a chain of six silicon atoms. The carbon halides, too, are more stable than those of silicon; and the oxides are gases, whereas those of the other elements of the sub-group are solids, the oxides SiO_2 and SnO_2 possessing high molecular complexity.

The study of carbon compounds will here be limited to such as illustrate analogies or specific differences, valuable for comparison between this element and other members of the group.

Germanium is more metallic in its physical properties than silicon, but shows some resemblance to this element in chemical properties. It burns in the air, forming the dioxide; like silicon, it is insoluble in hydrochloric acid, but soluble in hot caustic alkalis; like tin it forms hydrated dioxide by the action of nitric acid. It forms unstable, volatile hydrides, GeH_4, Ge_2H_6, Ge_3H_8, and the solids, $(GeH)_x$, $(GeH_2)_x$.

The elements **tin** and **lead** are of a more pronounced metallic character, both in physical and chemical properties. They form organo-metallic compounds, and tin forms a volatile hydride, SnH_4, which is evolved with hydrogen during the electrolysis of stannous sulphate; whilst PbH_4 seems to be formed by the solution of a lead-magnesium alloy in dilute acids. Their oxides and halides are less acidic than those of the foregoing elements, and metallic properties predominate.

It will be convenient to study the chief compounds formed by these five elements in one system. There will thus be presented a view of the changes taking place in various types of compound on passing from distinctly non-metallic to distinctly metallic elements.

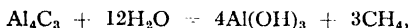
Hydrides (MH_4)

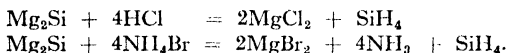
Carbon, silicon, and germanium are the only elements of the group which certainly form gaseous hydrides, and the above is the chief type common to the three elements.

Methane may be produced by direct synthesis; very small quantities of pure sugar charcoal are converted almost completely into methane when heated in hydrogen at 1150°.

The tetrahydrides of carbon and silicon may be produced by the action of water or acids on suitable carbides or silicides, just as nitrides, phosphides, sulphides, selenides, and tellurides yield the corresponding hydrides.

Aluminium carbide, for instance, yields methane thus:

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4,$$

and magnesium silicide and hydrochloric acid (or better, NH_4Br in liquid NH_3) give the corresponding hydride, silane,

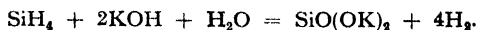
$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$
$$Mg_2Si + 4NH_4Br = 2MgBr_2 + 4NH_3 + SiH_4.$$

When ethyl orthosilicoformate, $SiH(OC_2H_5)_3$, prepared by the action of ethyl alcohol on silicochloroform, is heated with sodium,* silane and ethyl orthosilicate result,

$$4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OC_2H_5)_4,$$

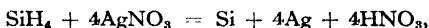
a reaction recalling the behaviour of phosphorous and hypophosphorous acids when heated (q.v.). Like methane, silicon hydride or silane is a gas, which, however, is more easily liquefied than methane. It differs from methane by being spontaneously inflammable in air, even at low temperature, or, like phosphine, under reduced pressure. It is less stable than methane, being dissociated at red heat. Though stable to pure water in quartz vessels, with alkali (even the alkali from glass) it yields silicate and hydrogen, a reaction which

* The sodium remains unchanged, its rôle in the reaction being unknown.

involves the separation of the hydride into its elements:

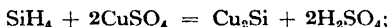
$$SiH_4 + 2KOH + H_2O = SiO(OK)_2 + 4H_2.$$

That SiH_4 should be less stable than CH_4, and GeH_4 less stable than SiH_4, is in accordance with the requirements of the periodic law that the stability of gaseous hydrides shall diminish with rise of atomic number in a group. This point is illustrated by comparing together, as regards stability, NH_3, PH_3, AsH_3, and SbH_3, BiH_3 being very unstable, as well as by contrasting H_2O with H_2S and HCl with HI.

Now unstable hydrides are reducing agents on account of the hydrogen which is liberated in their decomposition. It is true that the hydrides of some of the elements of the fifth group reduce by direct combination with oxygen, but this is due to the oxidizability of the elements themselves; it would hardly be expected, for example, that arsenic would be liberated in the free state by the oxidation of AsH_3; but in the case of H_2S and HI, sulphur and iodine are liberated, respectively, when the hydrogen with which they are combined is oxidized. The reaction between silicon hydride and silver nitrate, in which silicon and silver are precipitated,

$$SiH_4 + 4AgNO_3 = Si + 4Ag + 4HNO_3,$$

will now be understood, as well as the different behaviour of arsine towards the same reagent,

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 6HNO_3.$$

With less reducible substances, such as copper sulphate, silicides are precipitated,

$$SiH_4 + 2CuSO_4 = Cu_2Si + 2H_2SO_4;$$

this reaction being analogous to that with hydrogen sulphide.

Methane possesses no such reactivity as silane; the only hydrocarbon which possesses analogous properties is acetylene, C_2H_2, which reacts with silver and cuprous compounds, producing acetylides or carbides.

Like methane, silane undergoes metathesis with chlorine,

and when antimony pentachloride is used as a halogen carrier silicochloroform, $SiHCl_3$, is formed.

Other Hydrides

Carbon forms many other hydrides, the hydrocarbons, which are generally studied under organic chemistry.

Silicon also forms other hydrides or silanes; Si_2H_6, Si_3H_8, Si_4H_{10}, have been obtained pure, whilst Si_5H_{12} and Si_6H_{14} have probably also been prepared.*

Disilane, Si_2H_6, melts at $-132{\cdot}5°$ and boils at $-15°$; trisilane, Si_3H_8, melts at $-117°$ and boils at $53°$; tetrasilane, Si_4H_{10}, melts at $-90°$ and boils at $109°$ (approx.).

Solid, non-volatile, stable products, $(SiH)_x$, are known.

Halides MX_4

The type MX_4 is characteristic of the group, fluorides, chlorides, bromides, iodides, and mixed halides being known. The fluorides and chlorides afford the best comparative data.

Fluorides

CF_4	SiF_4	GeF_4	SnF_4	PbF_4
gas	gas	solid $+3H_2O$	volatile crystals	yellow powder.

Chlorides

CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
liquid B.P. 76°	liquid B.P. 56·9°	liquid B.P. 86°	liquid B.P. 113·9°	liquid decomposed by heat.

The **tetrafluorides** are formed by the direct union of the elements, and **carbon tetrafluoride,** the only carbon halide formed in this way, has been thus prepared.

They are generally obtained, however, by the action of hydrofluoric acid, derived from CaF_2 and H_2SO_4, upon the dioxides; for example,

$$SiO_2 + 4HF = SiF_4 + 2H_2O,$$

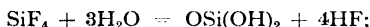
* *vide* Stock, *Hydrides of Boron and Silicon.*

or the corresponding alkali salts, stannates and plumbates, in which case the alkali double fluorides result, e.g.

$$K_2SnO_3 + 6HF = K_2SnF_6 + 3H_2O,$$

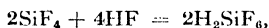
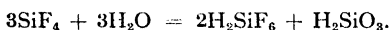
from which the fluorides themselves are separated by concentrated sulphuric acid.

The halanhydride character of **silicon tetrafluoride** is shown by its reaction with water, when silicic and hydrofluoric acids are formed,

$$SiF_4 + 3H_2O = OSi(OH)_2 + 4HF;$$

the hydrofluoric acid, however, combines with more silicon tetrafluoride, producing the stable **hydrofluosilicic acid,*** thus:

$$2SiF_4 + 4HF = 2H_2SiF_6,$$

the complete reaction being:

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3.$$

Of the **tetrachlorides**, that of carbon is not formed by direct union, but results as the final chlorine substitution product of methane or carbon disulphide; all the other elements, however, unite directly with chlorine, the compounds $SiCl_4$, $GeCl_4$, and $SnCl_4$ being thus prepared.

Silicon tetrachloride also results from the action of chlorine on a heated mixture of carbon and silicon dioxide,

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO,$$

whilst **germanium** and **tin tetrachlorides** are formed by distilling together the metal and mercuric chloride. **Lead tetrachloride** is produced in solution when chlorine is passed through hydrochloric acid in which lead dichloride is suspended. **Ammonium plumbichloride,** $(NH_4)_2PbCl_6$, is precipitated from this solution on adding ammonium chloride, and when this salt is decomposed by cold concentrated sulphuric acid, $PbCl_4$ separates as an unstable liquid.

The distinguishing characteristic of the tetrachlorides is that they are chloranhydrides rather than salts; thus they

* Boron trifluoride (q.v.) combines similarly with HF.

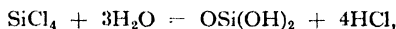
are volatile liquids, whilst typical salts are relatively non-volatile solids; they are unacted on by cold concentrated sulphuric acid, and, whilst soluble in non-hydroxylic solvents do not dissolve without change in water, but are decomposed by it, or by alkalis, with formation of the acidic hydroxides $M(OH)_4$, or $OM(OH)_2$, or their salts.

Carbon tetrachloride presents an anomalous character, being, like the hydride, comparatively inert; it is insoluble in, and not acted on by, water, but the prolonged action of potassium hydroxide gives carbonate and chloride,

$$CCl_4 + 6KOH = K_2CO_3 + 4KCl + 3H_2O,$$

a reaction which reveals the relationship of carbon tetrachloride to carbonic acid.

Silicon tetrachloride is at once decomposed by water, giving silicic and hydrochloric acids,

$$SiCl_4 + 3H_2O = OSi(OH)_2 + 4HCl,$$

but the chlorides $SnCl_4$ and $PbCl_4$ are capable of forming crystallohydrates, those of tin containing from three to eight molecules of water. The chlorides $SnCl_4$, $GeCl_4$, and $PbCl_4$ are moderately stable in aqueous solution when an excess of hydrochloric acid is present, but in dilute solution, and in the absence of much hydrochloric acid, they are decomposed like silicon tetrachloride.

Various double halides of the type R_2MX_6, derived from the acids H_2MX_6, are known in the case of the elements of Group IV B, as well as of IV A, some of which have been referred to in the preceding paragraphs. Of these the best known are the fluorides, though chlorides and bromides, but not iodides, exist. Carbon forms no such compounds on account of the inertness of its halides, and silicon forms only fluorides, that is H_2SiF_6 and its salts. Tin and lead, as well as thorium, the most metallic elements of the group, form double chlorides such as are not formed by the more non-metallic elements.

Oxychlorides

Just as chlorides or chloranhydrides of the type MCl_4 are the chlorides of the orthoacids $M(OH)_4$, so oxychlorides of the type $MOCl_2$ are the chlorides of the meta-acids $MO(OH)_2$.

Carbonyl chloride, $COCl_2$, known as phosgene gas, is formed by the union of carbon monoxide and chlorine under the influence of light and catalysts. It boils at 8°, is decomposed by water into CO_2 and HCl, after the manner of acid chlorides, and with ammonia forms carbamide or urea, $CO(NH_2)_2$.

The analogous silicyl chloride is not known. Si_2OCl_6, however, formed when $SiCl_4$ exchanges some chlorine for oxygen at high temperature, is a fuming liquid, boiling at 137°, and easily decomposed into silicic and hydrochloric acids.

$GeOCl_2$ is formed when $GeHCl_3$ is oxidized; $SnOCl_2$ results from the oxidation of $SnCl_2$; $PbOCl_2$ is unknown.

Derivatives of the Type MHX_3

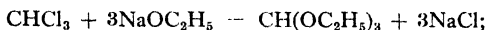
Trihalide derivatives of the hydrides CH_4, SiH_4, and GeH_4 are analogous. Since $CHCl_3$, the chloranhydride of orthoformic acid, $CH(OH)_3$, is known as chloroform, the analogous silicon and germanium compounds, as well as the bromine and iodine derivatives, receive similar names. The following substances of the type MHX_3 are known,* and are formed in the case of silicon and germanium, when the elements are heated in a stream of hydrogen halide gas.

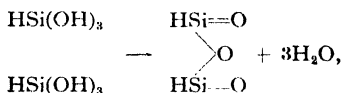
	C	Si	Ge
$MHCl_3$ ..	chloroform $CHCl_3$ B.P. 61°	silicochloroform $SiHCl_3$ B.P. 31·8°	germanium chloroform $GeHCl_3$ B.P. 72°
$MHBr_3$ ..	bromoform $CHBr_3$ B.P. 151°	silicobromoform $SiHBr_3$ B.P. 109–111°	?
MHI_3 ..	iodoform CHI_3 M.P. 119°	silicoiodoform $SiHI_3$ B.P. 106°/14 mm.	?

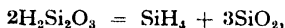
* Silicofluoroform, $SiHF_3$, likewise exists as a colourless gas, condensing at –80°.

It will be seen that, as in the case of the tetrahalides, the boiling-points of the silicon compounds are consistently lower than those of the corresponding carbon compounds, but that with germanium as shown by the chloroform the boiling-points of the compounds rise again.

Just as $CHCl_3$ corresponds with $CH(OH)_3$, the hypothetical orthoformic acid, into derivatives of which it is converted by sodium alcoholates, thus:

$$CHCl_3 + 3NaOC_2H_5 = CH(OC_2H_5)_3 + 3NaCl;$$

so **silicochloroform**, $SiHCl_3$, formed by heating silicon in hydrogen chloride gas, corresponds with $SiH(OH)_3$ and its alkyl compounds. Thus alcohol itself, without the use of sodium, forms ethyl orthosilicoformate, $SiH(OC_2H_5)_3$, a change which shows $SiHCl_3$ to be more reactive than $CHCl_3$, just as $SiCl_4$ is more reactive than CCl_4. Silicochloroform also is slowly hydrolyzed by water, which does not decompose chloroform, the product being **leucone**, or orthosilicoformic acid, $SiH(OH)_3$; the corresponding carbon compound does not exist. Leucone is, however, rather unstable, easily losing water; thus:

$$\begin{matrix} HSi(OH)_3 \\ \\ HSi(OH)_3 \end{matrix} = \begin{matrix} HSi{=}O \\ \rangle O \\ HSi{=}O \end{matrix} + 3H_2O,$$

the resulting product being known as silicoformic anhydride. This is, however, a neutral substance which is broken up by heat into silicon, hydrogen, and silicon dioxide, a reaction probably preceded by the formation of SiH_4,

$$2H_2Si_2O_3 = SiH_4 + 3SiO_2,$$

the hydride then decomposing thus, $SiH_4 = Si + 2H_2$.

Higher Chlorides of Silicon

When comparing the elements carbon and silicon it was shown that silanes of the type Si_nH_{2n+2}, corresponding with the paraffin hydrocarbons, exist in which n may be

1, 2, 3, 4, 5, or 6. A similar series of chlorides is known,* viz.:

$SiCl_4$	Si_2Cl_6	Si_3Cl_8	Si_4Cl_{10}	Si_5Cl_{12}	Si_6Cl_{14}
B.P. 56·9°	B.P. 146–148°	B.P. 215–218°	B.P. 149–151° (15 mm.)	B.P. 190° (15 mm.)	Solid M.P. 170°.

The higher chlorides are obtained together with $SiCl_4$ when chlorine is passed over 50 per cent ferro-silicon heated to 180–200°. According to Martin† they are formed in the order of diminishing complexity by the chlorination and disruption of chains of silicon atoms.

Si_2Cl_6 is hydrolyzed by water, producing silico-oxalic acid, analogous to oxalic acid:

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O=Si—OH        O=C—OH
  |       :      |
O=Si—OH        O=C—OH,
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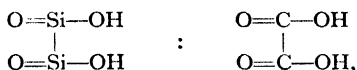
and Si_3Cl_8, under similar conditions, gives silicomesoxalic acid:

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   O=Si—OH            O=C—OH
     |                  |
HO—Si—OH     :     HO—C—OH
     |                  |
   O=Si—OH            O=C—OH
silicomesoxalic acid   mesoxalic acid
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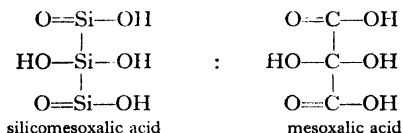
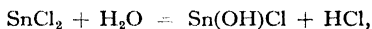

Halides MX_2

Halides of the type MX_2 are unknown with carbon and silicon, but are represented in the case of germanium, tin, and lead. Germanous halides possess no saline properties, but stannous and lead halides are important compounds which manifest definitely saline characters, being prepared by the methods usually available for the formation of salts, for example, in the case of tin, by the action of the halogen acid on the metal, as well as by its action on the monoxides in the case of tin and lead, and by precipitation of salts of

* Besson and Fournier, *Compt. rend.*, 1909, **148**, 839; **149**, 34; 1910, **151**, 1055.
† Martin, *Chem. Soc. Trans.* (1914), **105**, 2836.

the latter metal, whose halides are but slightly soluble in water.

Chloranhydride characters are manifested strongly by **germanous chloride,** slightly by **stannous chloride,** but scarcely at all by **lead chloride.** For example, stannous chloride is somewhat soluble in ether, whilst lead chloride is insoluble, and stannous chloride melts at a lower temperature than lead chloride; also, whilst stannous chloride is decomposed by excess of water according to the reaction,

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl,$$

lead chloride is not so decomposed, although basic salts are formed by combination with PbO. Both chlorides form double salts with alkali chlorides, the chief of which correspond to the acid type H_2MCl_4; the acid H_2SnCl_4, as well as $HSnCl_3$, probably exists in a solution of stannous chloride in hydrochloric acid. Lead chloride, bromide, and iodide show progressive insolubility in cold water, in which they resemble mercuric and silver halides; they are, however, easily soluble in hot water, differing in this respect from the silver halides and mercuric iodide.

Oxides of the Type MO_2

These, corresponding with the maximum oxygen valency of the group, are known for each element. **CO_2, SiO_2, GeO_2,** and **SnO_2** are the products of the direct union of the elements with oxygen, and GeO_2 and SnO_2 are formed by the action of nitric acid on the elements; CO_2, SiO_2, and SnO_2 occur naturally in the free state, and CO_2 and SiO_2 combined in the form of carbonates and silicates. **PbO_2** is not the most stable oxide of lead, being obtained, not by the combustion of the metal, but by the oxidation of the monoxide, e.g. by hypochlorite solution, $PbO + NaOCl = PbO_2 + NaCl$; and being reconverted into the monoxide by heat.

A comparison of the physical properties of these oxides

reveals a great contrast between gaseous carbon dioxide on the one hand, and on the other solid silica, existing in the amorphous and two crystalline forms of quartz and tridymite, together with the solid dioxides of germanium, tin, and lead. Silica melts at a very high temperature; it can, however, be melted, and even vaporized, in the electric furnace. Molten silica may be worked like glass, and made into tubes or flasks, which are useful because, on account of the minute coefficient of expansion of the substance, they are not fractured by sudden changes of temperature.

Inasmuch as the chlorides of silicon are more volatile than the corresponding carbon compounds, this great difference in properties between CO_2 and SiO_2 must be attributed to the polymerization of the latter substance, which is known to possess a highly condensed crystal structure $(SiO_2)_x$.

Each of these oxides is acidic, giving rise to a weak acid of the type $M(OH)_4$ or $MO(OH)_2$; lead dioxide, however, must be regarded also as a basic peroxide, since although with alkali hydroxides plumbates such as K_2PbO_3 are formed, the action of acids produces salts corresponding with the basic oxide PbO, oxygen or its equivalent being set free. In this respect lead is analogous to its neighbour in series, bismuth, whose pentoxide behaves as a basic peroxide as well as a feebly acidic oxide. The plumbic salts $Pb(C_2H_3O_2)_4$ and $Pb(SO_4)_2$, however, exist.

Orthoacids

Of the orthoacids, $M(OH)_4$, **orthosilicic acid**, H_4SiO_4, may exist in solution, and **orthostannic acid**, H_4SnO_4, can be precipitated by alkali hydroxide from a solution of stannic chloride, or by the hydrolysis of ammonium stannate caused by boiling; the others are unknown. Organic orthocarbonates are represented by $C(OC_2H_5)_4$, orthosilicates by $Si(OC_2H_5)_4$, and the minerals olivine, Mg_2SiO_4, and zircon, $ZrSiO_4$; red-lead, $Pb_3O_4(Pb_2PbO_4)$, may also be referred to the same type, since PbO_2 is separated from it by nitric acid. Orthostannates

of calcium, cobalt, and nickel are said to have been prepared by heating mixtures of the corresponding oxides; calcium orthoplumbate, Ca_2PbO_4, occurs crystalline.

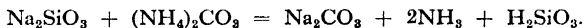
Meta-acids

Meta-acids of the type $MO(OH)_2$ are represented by **carbonic acid,** H_2CO_3, which exists in dilute aqueous solution; **metasilicic acid,** H_2SiO_3, which is approximately the composition of air-dried " gelatinous silica " precipitated from a strong solution of an alkali silicate by acid; so-called α-stannic acid, better known as α-**metastannic acid,** H_2SnO_3, similarly obtained from a stannate by the action of an acid, or by the decomposition of stannic chloride by water in presence of calcium carbonate; and H_2PbO_3, which is deposited at the anode in the electrolysis of an alkaline solution of a lead salt.

Of the salts derived from the meta-acids, $MO(OH)_2$, the **carbonates,** really metacarbonates, are well known; of the alkali **metasilicates,** Na_2SiO_3 has been obtained crystallized with 3, 6, and 9 H_2O; " soluble glass ", prepared by fusing sodium carbonate with from two to three equivalents of silica, is obtained as a solid or a colloidal solution; Wollastonite, $CaSiO_3$, is a naturally crystallized metasilicate. The **metastannates,** or α-stannates, K_2SnO_3 and Na_2SnO_3, are obtained as crystalline tri-hydrates by evaporating the solution of the hydrated dioxide in alkali hydroxide. They are considered to be hydroxo-salts of the type $M_2[Sn(OH)_6]$. Potassium **metaplumbate,** K_2PbO_3, $3H_2O$, or $K_2[Pb(OH)_6]$, is a crystalline salt. Pb_2O_3 is lead metaplumbate, $PbPbO_3$; from each of these compounds lead dioxide is separated by acid. The salts of these acids are easily hydrolyzed by water or dilute mineral acids, because the acids themselves are very weak; when the acids are separated by hydrolysis they readily break up into the anhydrides and water, as in the case of carbonic acid, or yield partially hydrated and complex dehydration products.

Silicic acid is so weak an acid that its ammonium salt, like

the corresponding stannate, is hydrolyzed by water; and this fact accounts for the separation of gelatinous silica when ammonium carbonate or other ammonium salt is added to a solution of a silicate; thus:

$$Na_2SiO_3 + (NH_4)_2CO_3 = Na_2CO_3 + 2NH_3 + H_2SiO_3.$$

It cannot be said that definite compounds corresponding with the formulæ H_4SiO_4 and H_2SiO_3 exist. The facts are more nearly represented by the formulæ mSiO$_2$, $2n$H$_2$O and mSiO$_2$, nH$_2$O, where m and n are nearly equal; indeed doubt has been thrown on the existence of definite hydrates of silica.

When gradually heated, gelatinous silica loses water and becomes less soluble, until by ignition highly polymerized "insoluble silica" is produced.

When acid is added to a dilute solution of sodium silicate, no precipitate is formed, the silicic acid forming a colloidal solution. The difference between this behaviour and that of a more concentrated solution is dependent not solely on concentration, but upon the existence of the hydrated silica in the state of colloidal **hydrosol**. This state persists when the solution is dialysed so that a concentrated hydrosol is formed, which, however, is not a true solution, but a suspension of ultramicroscopic particles. By catalytic action this hydrosol is converted into the corresponding **hydrogel**, which is thus a different form of the same product.

Such a gel containing 300 molecules of water to each SiO_2 behaves like a viscous liquid: with 6 molecules of water it can form a dry powder, a condition not to be mistaken for the complete dehydration required in analytical procedure.

When purified by dialysis, and dried at 250°–300° the highly adsorbent properties of the gel render it of considerable importance for removing, e.g. sulphur compounds from petroleum distillates and water from blast furnace air. The adsorbed substance may be recovered and the adsorbent regenerated by heating.

As a weak acid, silicic acid also forms salts of great com-

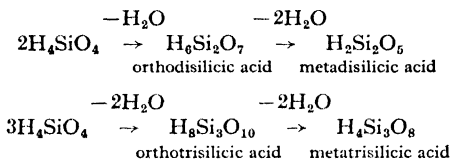
plexity, so that the types of metallic silicates are numerous. Other feeble acids show the same tendency, for instance, boric, tungstic, molybdic, and chromic acids.

Metallic silicates cannot be prepared by precipitation with alkali silicates, for hydroxides and hydrous silica are the main products. They may be prepared by fusing mixtures of the oxide and silica, the cooled product generally forming a glass.

Structure of Silicates

The systematic chemistry of the silicates offers a difficult problem. In the simpler cases, the empirical formulæ, derived from analyses, enabled them to be classified tentatively as derivatives of orthosilicic acid, H_4SiO_4, or metasilicic acid, H_2SiO_3, or of complex silicic acids derived therefrom by condensation and elimination of water, thus:

$$2H_4SiO_4 \xrightarrow{-H_2O} \underset{\text{orthodisilicic acid}}{H_6Si_2O_7} \xrightarrow{-2H_2O} \underset{\text{metadisilicic acid}}{H_2Si_2O_5}$$

$$3H_4SiO_4 \xrightarrow{-2H_2O} \underset{\text{orthotrisilicic acid}}{H_8Si_3O_{10}} \xrightarrow{-2H_2O} \underset{\text{metatrisilicic acid}}{H_4Si_3O_8}$$

The structure of more complex natural silicates could not be derived thus, for, by reason of their refractory character and insolubility, no information was available regarding their molecular condition. It was not until W. L. Bragg and his co-workers in brilliant fashion attacked the problem by X-ray analysis of the solid structures, that an accurate basis for systematic treatment was obtained; Goldschmidt and Pauling contributing on the theoretical side.

Ionic Structures.—The fundamental structures of silicates are the tetrahedral grouping of four oxygen atoms round each silicon atom, and the linking of tetrahedra through apical oxygen atoms. If the tetrahedron be also an ion, $SiO_4^{\equiv}$, its formation is only possible if four electrons (marked ×) are acquired, and its behaviour is consistent with the localization of one negative charge on each oxygen atom.

```
     • x
     :O:
  •• •• ••                   |  ••  |
 ˣ:O:Si:O:ˣ ,   and      —Si:O:Si—.
  •• •• ••                   |  ••  |
     :O:
     • x
```

A crystal containing these negative oxygen atoms will be neutral if positive ions of suitable charge are inserted at appropriate points. These positive ions are " co-ordinated " by the oxygen atoms, the term referring simply to the spatial disposition of the oxygen atoms round the ions, and not implying the co-ordinate link of Sidgwick.

The ion $(SiO_4)^{=}$ is the simplest structure, and exists as such in orthosilicates, e.g. *zircon*, $ZrSiO_4$, *garnet*, $Ca_3Al_2(SiO_4)_3$, *topaz*, $Al_2F_2SiO_4$, and *olivine* $(Mg, Fe^{II})SiO_4$.

In olivine, X-ray analysis reveals that the $[SiO_4]^{\equiv}$ ions are linked electrostatically by the positive Mg^{++} ions (which may be replaced by Fe^{++}), each Mg^{++} ion being surrounded, or co-ordinated, by six oxygen atoms. By this means, $2/6 = 1/3$ of the field due to each oxygen atom is neutralized. Complete neutralization is achieved by the lattice structure allowing three Mg^{++} ions round each oxygen atom.

In garnet each calcium or aluminium ion is surrounded by eight and six oxygen atoms, respectively. Ca^{++} may be replaced by Mg^{++} or Fe^{++}, and Al^{+++} by tervalent iron or chromium.

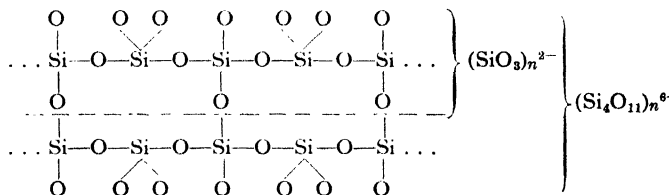
Further development of independent groups arises when two, three, four, or six tetrahedra are linked through apical oxygen atoms; such bonding atoms are neutral and play no part in co-ordinating positive ions.

The three ions illustrated below are present respectively in *melilite*, $Ca_2MgSi_2O_7$, *benitoite*, $BaTiSi_3O_9$, and *beryl*, $Be_3Al_2Si_6O_{18}$, the only example known to contain this ring. Again these groups are bound in the crystal by co-ordination of the positive ions by the charged oxygen atoms.

Here the beryllium ion is the centre of a tetrahedral arrangement of oxygen atoms, while for Al^{+++} the arrangement is octahedral.

$(Si_2O_7)^{6-}$ $(Si_3O_9)^{6-}$ $(Si_6O_{18})^{12-}$

Chain Structures.—By extending the Si_2O_7 group, a chain structure is developed, which by duplication may form a band structure, both being co-extensive with the dimensions of the crystal; no ions or molecules exist. The silicon oxygen ratios in the two structures give the formulæ $(SiO_3)_n$ and $(Si_4O_{11})_n$, respectively.

```
     O      O  O      O      O  O      O
     |       \/       |       \/       |
 . . . Si—O—Si—O—Si—O—Si—O—Si . . .       } (SiO3)n 2-
     |                |                |
     O                O                O             } (Si4O11)n 6-
 - - | - - - - - - - -| - - - - - - - -|
     |                |                |
 . . . Si—O—Si—O—Si—O—Si—O—Si . . .
     |       /\       |       /\       |
     O      O  O      O      O  O      O
```

Correctly projected, each triad of atoms, —Si—O—Si—, in the band structure, will lie on the sides of a hexagon.

When such chains or bands are linked by positive ions the resulting structure shows a fibrous cleavage, as in *diopside*, $CaMg(SiO_3)_2$ and *chrysotile*, $(OH)_6Mg_6Si_4O_{11}, H_2O$. The latter is a source of commercial asbestos.

Sheet Type.—By an extension of the band structure upwards and downwards, sheets of hexagonal rings will be obtained in which each Si atom will have one singly bound

oxygen, and giving the formula $(Si_2O_5)_n^{2-}$. Such laminar structures occur in *talc*, $Mg_3(OH)_2Si_4O_{10}$, and in *muscovite mica*, $K(OH)_2Al_2[(AlSi_3)O_{10}]$. Their extended silicon sheets are cemented in pairs by Mg^{++} and Al^{+++} ions, respectively, which are bound to the charged O atoms and OH ions. In talc, the resulting neutral sandwich structures are weakly held together in the mass: in mica, they are more firmly bound by the K^+ ions required to neutralize the structure.

Net Structures.—If all four oxygen atoms are used to link tetrahedra then the resulting three-dimensional network is neutral silica itself $(SiO_2)_n$.

Aluminium may be present in silicates as the positive ion, Al^{+++}, or it may replace silicon in fourfold co-ordination with oxygen, still maintaining the ratio $(M_xO_y)_n$ (cf. mica above). This change from SiO_4 to AlO_4, however, requires an additional electron, and this in general is compensated by suitable positive ions. From $(SiO_2)_n$ we may derive, therefore, such aluminosilicates as the felspars, *orthoclase*, $K(Al\ Si_3)O_8$, *albite*, $Na(AlSi_3)O_8$, *anorthite*, $Ca(Al_2Si_2)O_8$.

In the *zeolites*, a similar but more open network allows the retention of loosely held water molecules. These minerals are valuable for their base exchange reaction utilized in the " Permutite " process of water softening. One example is *natrolite*, $Na_2(Al_2Si_3)O_{10}$, $2H_2O$.

The *ultramarines* and related minerals possess the ideal framework $(Al_6Si_6O_{24})^{6-}$, i.e. $(MO_2)_{12}$. Cavities in this structure contain eight Na^+ ions (which are replaceable by other cations), the excess positive charge being neutralized by similarly placed anions, such as $S_2^{=}$, $S_3^{=}$, $SO_4^{=}$ or Cl^-.

Various complex **stannic acids** and their salts have been reported, but some of the reactions noted below are probably due to colloidal SnO_2 of varying particle size and water content.

In addition to the metastannic acid, or α-stannic acid, which was mentioned above, a polymer, generally described as **β-metastannic acid**, or **β-stannic acid**, is formed by

the action of moderately concentrated nitric acid on tin. Stannic nitrate is probably first produced, but being unstable decomposes into oxides of nitrogen and an insoluble cream-white powder possibly having the composition indicated below.

By the action of cold sodium hydroxide solution on β-stannic acid a crystalline powder having the composition $Na_2Sn_5O_{11}$, $4H_2O$ is formed; the potassium salt, also, is $K_2Sn_5O_{11}$, $4H_2O$. Thus β-stannic acid, which when air-dried has the empirical composition SnO_2, $2H_2O$, becomes $H_2Sn_5O_{11}$, $9H_2O$; and the acid dried in a vacuum, having the composition SnO_2, H_2O, is $H_2Sn_5O_{11}$, $4H_2O$ or $Sn_5O_9(OH)_2$, $4H_2O$, corresponding with the alkali salts. By the action of hydrochloric acid on β-stannic acid a chloride having the composition $5SnO_2$, $2HCl$, $3H_2O$ is formed; this is β-stannyl chloride: $Sn_5O_9Cl_2 \cdot 4H_2O$, the chloride of β-stannic acid. Prolonged action of hydrochloric acid on β-stannic acid produces stannic chloride, $SnCl_4$, and concentrated potassium-hydroxide solution similarly forms potassium α-stannate, K_2SnO_3, these polymeric varieties of stannic acid being broken down by such treatment.

Thus stannic oxide resembles silica in being the parent substance of various complex acids and salts, though it differs from it in possessing distinctly basic properties; stannic acid, like silicic acid, can also exist in the colloidal state, but in such a condition is very unstable.

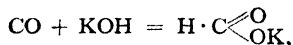
Oxides of the Type MO and their Derivatives

The type MO is represented by the oxides **CO, SiO,* GeO, SnO,** and **PbO.** CO is generally regarded as a neutral oxide, GeO is little known, SnO and PbO are feebly basic oxides, which are obtained in hydrated form from their salts by precipitation. As might be expected, these salts show a tendency to be hydrolyzed by water, giving rise to basic salts.

* SiO is said to be obtained as a by-product in the preparation of carborundum in the electric furnace. It results from the reduction of silica by carbon, and is described as a red powder with reducing properties. H. N. Potter, *Electrochem. and Met. Ind.* (1907), **5**, 442.

The hydrated oxides also exhibit acid properties by reason of their solubility in excess of alkali hydroxide solutions.

Carbon Monoxide.—The relationship of carbon monoxide to formic acid is interesting. Although carbon monoxide does not yield that acid with water, it is gradually absorbed by strong potassium hydroxide, producing potassium formate,

$$CO + KOH = H \cdot C\begin{matrix} \nearrow O \\ \searrow OK \end{matrix},$$

and might therefore be considered the anhydride of formic acid, especially also as it is obtained when the acid is dehydrated by means of sulphuric acid. An inspection of the constitution of the oxide and acid shows, however, that formic acid is not hydroxylated carbon monoxide, which would be $C\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}$; thus combination of the oxide with potassium hydroxide involves a molecular rearrangement, as is shown in the above equation. Only in a limited and unusual sense, then, can carbon monoxide be considered the anhydride of formic acid.

Stannous oxide, SnO, is a black powder, obtained by igniting the hydrated oxide out of contact with air.

The hydroxide $Sn(OH)_2$ is said not to exist, for the white precipitate formed by the addition of alkali hydroxide or carbonate solution to a solution of a stannous salt is $Sn_2O(OH)_2$; this dissolves in excess of alkali hydroxide, forming a stannite which is not $Sn(OM)_2$ but $M \cdot [HSnO_2]$, a salt whose monohydrate is a hydroxo-salt $M \cdot [Sn(OH)_3]$; thus SnO exhibits both basic and acidic properties like alumina. **Stannous sulphate** and **nitrate** are formed by the action of the dilute acids on tin or hydrated stannous oxide, and are very easily hydrolyzed by water. Stannous carbonate is unknown.

Lead monoxide, PbO, known as litharge or massicot, is the most stable oxide of lead, resulting when either of the other oxides is ignited strongly in air. It is fusible and may be obtained crystalline. The hydroxide exists in the forms $Pb_2O(OH)_2$ and $Pb_3O_2(OH)_2$, and is slightly soluble in water,

to which it imparts an alkaline reaction. It is formed in solution when water containing dissolved oxygen acts on metallic lead. In spite of the basic properties indicated by its alkaline reaction, lead hydroxide, when precipitated from a lead salt by alkali hydroxide, dissolves in excess of the reagent, producing plumbite hydroxo-ions, $[Pb(OH)_3]^-$, $[Pb(OH)_4]^=$ and $[Pb(OH)_6]^{\equiv}$.

Since lead is more basigenic than tin, its oxysalts, derived from PbO, are more stable than the stannous oxysalts. **Lead sulphate**, $PbSO_4$, is nearly insoluble in water; consequently the action of dilute sulphuric acid on lead, with the evolution of hydrogen, is soon arrested by the formation of a crust of sulphate upon the metal; lead, however, dissolves in warm, concentrated sulphuric acid, forming an acid sulphate, thus:

$$Pb + 3H_2SO_4 = Pb(HSO_4)_2 + SO_2 + 2H_2O;$$

this salt is hydrolyzed by water, $PbSO_4$ being precipitated. In its insolubility in water and its solubility in concentrated sulphuric acid, as well as by reason of isomorphism, this salt closely resembles barium sulphate. **Lead nitrate**, $Pb(NO_3)_2$, formed by dissolving the metal or the oxide in nitric acid, crystallizes in regular octahedra, isomorphous with barium nitrate. Its aqueous solution shows but a faintly acid reaction; basic salts, such as $Pb(OH)NO_3$, are formed when the solution is digested with lead monoxide. A further resemblance between lead and barium is shown in the properties of the chromates, both of which are yellow solids insoluble in water and acetic acid. This resemblance, however, does not extend to chemical properties· it is not generic, as the hydrolysis and solution of lead chromate by alkali hydroxide, owing to the acidic properties of lead hydroxide, whilst barium chromate is insoluble in this reagent, is sufficient to indicate. It may here be pointed out that no true conclusion as to the relationships between elements can be drawn from a consideration of the physical properties of their compounds alone. The chemical differences between barium and lead and their compounds require the elements to be placed in different categories,

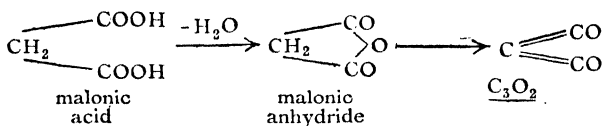
apart altogether from the indications of the periodic law.

Lead carbonate, $PbCO_3$, is precipitated when alkali-bicarbonate solution is added to a lead salt, a basic carbonate resulting when the normal carbonate solution is used. White-lead is the basic carbonate, $2PbCO_3, Pb(OH)_2$. The native form of lead carbonate, cerussite, is isomorphous with barium carbonate, but except for their insolubility in water there is no further resemblance between the two salts. Tin, being less basigenic than lead, forms no carbonate.

SUBOXIDES

Carbon suboxide,* C_3O_2, a volatile liquid, B.P. 6°, is derived from malonic acid by dehydration thus:

$$CH_2\begin{cases}COOH\\COOH\end{cases} \xrightarrow{-H_2O} CH_2\begin{cases}CO\\CO\end{cases}\!>O \longrightarrow C\begin{cases}=CO\\=CO\end{cases}$$

malonic acid — malonic anhydride — C_3O_2.

Electron diffraction experiments show that the molecule is linear. It is a ketene which combines with two molecules of formic acid to give $\begin{matrix}HOOC\\HO\end{matrix}\!>C:C:C<\!\begin{matrix}COOH\\OH.\end{matrix}$

Carbon suboxide combines with water, hydrogen chloride, and ammonia, to form malonic acid, malonyl chloride, and malonamide, respectively. It polymerizes slowly to a red solid at 15°, more rapidly at 200° when gaseous *dicarbon*, C_2, is also formed: $C_3O_2 = CO_2 + C_2$.

Lead suboxide, Pb_2O, is the first product of the oxidation of lead, and is obtained as a black powder when lead oxalate is heated out of contact with oxygen:

$$2PbC_2O_4 = Pb_2O + CO + 3CO_2.$$

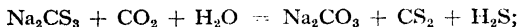
When heated, this oxide decomposes into lead and monoxide; but by interaction with alkyl halides it yields lead subhalides.

* Diels and Wolf, *Ber.* (1906), **39**, 689; Stock and Stoltzenberg, *Ber.* (1917), **50**, 498.

SULPHIDES

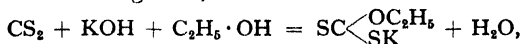
The sulphides of the group resemble the oxides in chemical properties. The more important are **CS_2**—together with **COS**—**SnS, SnS_2,** and **PbS.** A gradation of properties may be observed in these sulphides similar to that which obtains in the oxides, though, as in other groups, the sulphides are distinctly less acidic than the corresponding oxides. Carbon and tin disulphides dissolve in alkali sulphide solutions, forming thiocarbonates and thiostannates respectively. With alkali hydroxides, mixtures of thio- and oxysalts result, or salts of the oxyacids in which oxygen is partially replaced by sulphur. Lead sulphide is insoluble in alkali hydroxides and sulphides, which fact, considering that lead hydroxide is soluble in potassium-hydroxide solution, illustrates the more feebly acidic character of the sulphide. The difference of behaviour of lead and tin sulphides towards alkalis serves to separate the metals in analysis.

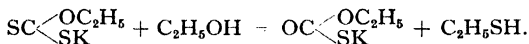
Carbon disulphide, CS_2, boils at 46° under atmospheric pressure, the boiling-point of CO_2 being −78°. As thiocarbonic anhydride, carbon disulphide might give rise to two acids, orthothiocarbonic acid, H_4CS_4, and metathiocarbonic acid, H_2CS_3, and their salts. Salts of both acids exist, though those of the meta-acid are the more important. The meta-acid is known in the free state, and is produced as an unstable yellow oil, when an aqueous solution of sodium metathiocarbonate, formed by dissolving carbon disulphide in sodium-sulphide solution, is acidified. In accordance with the feebler character of the thio- as compared with the oxysalts, sodium metathiocarbonate is decomposed by carbon dioxide; thus:

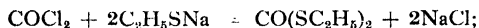
$$Na_2CS_3 + CO_2 + H_2O = Na_2CO_3 + CS_2 + H_2S;$$

and when boiled with water in an inert atmosphere it decomposes thus:

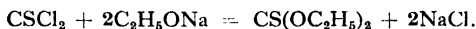
$$Na_2CS_3 = Na_2S + CS_2; \; Na_2S + 2H_2O = 2NaOH + H_2S.$$

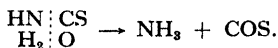
With alcoholic potassium hydroxide, CS_2 yields potassium xanthate or xanthogenate,

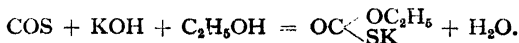
$$CS_2 + KOH + C_2H_5\cdot OH = SC\langle{}^{OC_2H_5}_{SK} + H_2O,$$

from which the acid itself, $SC\cdot OC_2H_5\cdot SH$, is separated as an unstable oil on acidifying; whereas by the action of excess of alcoholic potash, a sulphur atom is removed, and potassium ethyl monothiocarbonate results,

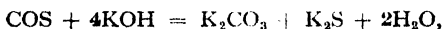
$$SC\langle{}^{OC_2H_5}_{SK} + C_2H_5OH = OC\langle{}^{OC_2H_5}_{SK} + C_2H_5SH.$$

Isomeric with the unknown, unsymmetrical dithiocarbonic acid, $SC\langle{}^{OH}_{SH}$, of which xanthic acid is the ethyl ester, is the symmetrical acid $OC\langle{}^{SH}_{SH}$, whose ethyl ester results from the action of sodium ethyl sulphide on carbonyl chloride:

$$COCl_2 + 2C_2H_5SNa = CO(SC_2H_5)_2 + 2NaCl;$$

similarly the isomer of the above monothiocarbonic acid $OC\langle{}^{OH}_{SH}$, namely $SC\langle{}^{OH}_{OH}$, is represented in the form of its ethyl salt, prepared by the action of sodium ethoxide on thiocarbonyl chloride:

$$CSCl_2 + 2C_2H_5ONa = CS(OC_2H_5)_2 + 2NaCl.$$

The gas, **carbon oxysulphide**, or carbonyl sulphide, results from the direct union of carbon monoxide and sulphur at high temperature, also from the hydrolysis of thiocyanic acid, liberated from its salts, by dilute sulphuric acid.

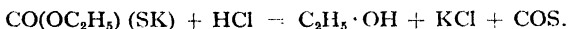
$$\begin{matrix} HN \vdots CS \\ H_2 \vdots O \end{matrix} \longrightarrow NH_3 + COS.$$

The oxysulphide dissolves in alcoholic potassium-hydroxide solution, forming potassium ethyl monothiocarbonate, in a manner entirely analogous to that by which xanthates are produced from carbon disulphide:

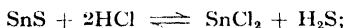
$$COS + KOH + C_2H_5OH = OC\langle{}^{OC_2H_5}_{SK} + H_2O.$$

When dilute aqueous potassium-hydroxide solution is used, potassium carbonate and sulphide are formed; thus:

$$COS + 4KOH = K_2CO_3 + K_2S + 2H_2O,$$

the wholly metallic monothiocarbonate,

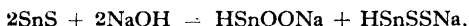
$$OC\begin{matrix}\diagup OK \\ \diagdown SK\end{matrix},$$

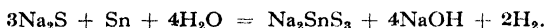
which might be expected, not being formed. Similarly the oxysulphide is slowly decomposed by water into CO_2 and H_2S. From ethyl monothiocarbonate, hydrochloric acid liberates the oxysulphide, thus:

$$CO(OC_2H_5)(SK) + HCl = C_2H_5 \cdot OH + KCl + COS.$$

Stannous sulphide, SnS, a dark-brown powder, insoluble in water, is decomposed by concentrated hydrochloric acid,

$$SnS + 2HCl \rightleftharpoons SnCl_2 + H_2S;$$

the metallic properties of tin are thus manifested, since less metallic sulphides such as arsenious sulphide, As_2S_3, are not attacked by this reagent.*

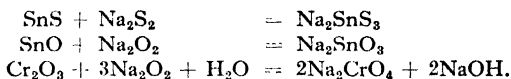
Stannous sulphide is soluble with some difficulty in sodium-hydroxide solution, even when the precipitate is finely divided; the following reaction takes place:

$$2SnS + 2NaOH = HSnOONa + HSnSSNa.$$

SnS is practically insoluble in dilute sodium-sulphide solution, but a concentrated solution of this reagent gradually decomposes it into SnS_2 and Sn, the former of which dissolves readily, and the latter slowly, giving off hydrogen, thus:

$$3Na_2S + Sn + 4H_2O = Na_2SnS_3 + 4NaOH + 2H_2.$$

Stannous sulphide easily dissolves in alkali polysulphides, including yellow ammonium sulphide, forming thiostannate, just as stannous oxide and chromic oxide dissolve in sodium-

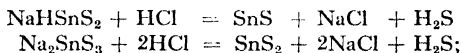
* With this may be compared the different behaviour of non-metallic and metallic chlorides towards sulphuric acid.

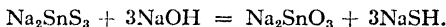
peroxide solution, forming sodium stannate and chromate respectively:

$$SnS + Na_2S_2 = Na_2SnS_3$$
$$SnO + Na_2O_2 = Na_2SnO_3$$
$$Cr_2O_3 + 3Na_2O_2 + H_2O = 2Na_2CrO_4 + 2NaOH.$$

Stannic sulphide, SnS_2, when prepared by subliming a mixture of tin, sulphur, and ammonium chloride, is known as mosaic gold; when precipitated it is a dull-yellow powder, which generally contains some hydrated dioxide. It dissolves easily in alkali sulphide and hydroxide solutions, thus showing superior acidic properties to SnS, and forming thiostannate and a mixture of stannate and thiostannate respectively.

Metathiostannic acid, H_2SnS_3, and its alkali salts, e.g. $Na_2SnS_3, 2H_2O$, exist in the solid state, and an orthosalt of the composition $Na_4SnS_4, 12H_2O$ has been prepared.

Acids decompose thiostannites and thiostannates, reprecipitating stannous or stannic sulphide:

$$NaHSnS_2 + HCl = SnS + NaCl + H_2S$$
$$Na_2SnS_3 + 2HCl = SnS_2 + 2NaCl + H_2S;$$

whilst alkalis convert them, as they do thiocarbonates, into oxysalts and alkali hydrosulphide:

$$Na_2SnS_3 + 3NaOH = Na_2SnO_3 + 3NaSH.$$

This reaction illustrates the superior stability and acidity of the oxides over the sulphides.

SUB-GROUP IV A

Titanium, Zirconium, Hafnium, and Thorium

The elements of sub-group IV A, titanium, zirconium, hafnium, and thorium, are more metallic than those of the B sub-group, and the metallic properties increase with rise of atomic weight in accordance with the requirements of the periodic law. As, however, was pointed out in the introduction to this group, the differences between analogous members

of the sub-groups are less in this than in any other group. The types of compounds formed in this sub-group are more numerous than in sub-group B.

Titanium occurs as TiO_2 in *rutile*, *brookite* and *anatase*: the main source is *ilmenite*, $FeTiO_3$. Zirconium occurs as *zircon*, $ZrSiO_4$, as ZrO_2, and in some silicates: in many instances associated with considerable amounts of hafnium. Thorium occurs as the silicate *thorite*, and in *monazite sand*, (Th, Ce, La, &c.), phosphates.

Hafnium.—In 1911 G. Urbain claimed to have discovered *celtium* in some lutecium-ytterbium residues, but the claim was not substantiated. In May, 1922, Dauvillier examined the X-ray spectrum of these residues, and detected element 72. Urbain claimed that this was celtium, but the isolation of the element was doubtful. In January, 1923, D. Coster and G. von Hevesy reported the discovery of element 72 in zirconium minerals, and named it *hafnium*, Hf, from Hafnia, an ancient name for Copenhagen.

The new element is a metal not of the rare-earths, but of the zirconium family, and, notwithstanding Urbain's claim for celtium, the name hafnium has been adopted for it. It is found in zirconium minerals from various parts of the world, and in commercial zirconium preparations. It is estimated to constitute more than 0·002 per cent of the earth's crust, zirconium constituting 0·017 and thorium 0·002 per cent.

Hafnium and zirconium may be separated by fractional precipitation of their phosphates or by crystallizing the oxychlorides, $MOCl_2$, the salts of hafnium being less soluble in both cases in acid solution. A better separation is effected by fractionally crystallizing the ammonium or potassium hexafluorides, the hafnium salts being the more soluble.

The two metals may be obtained by reducing their complex alkali fluorides, or their tetrachlorides by sodium or potassium. Titanium is produced by similar methods.

$$K_2MF_6 + 4K = 6KF + M.$$

Hafnium may be purified by decomposing the volatile HfI_4 by a glowing tungsten wire. It is of use in tungsten filament manufacture.

The following **oxides** are known:

	Ti	Zr	Hf	Th
M_2O_2	Ti_2O_2	—	—	—
M_2O_3	Ti_2O_3	Zr_2O_3	—	—
MO_2	TiO_2	ZrO_2	HfO_2	ThO_2
M_2O_5	—	Zr_2O_5	—	—
MO_3	TiO_3	ZrO_3	HfO_3	—
M_2O_7	—	—	—	Th_2O_7

Of the **typical oxides, TiO_2** is trimorphous and amphoteric, dissolving in sulphuric acid, and yielding titanate by alkali fusion, it is valued as a white pigment because of its great covering power; **ZrO_2** is also amphoteric, but more basic than TiO_2, it is refractory and may be employed for making crucibles to be heated to 2000°; **HfO_2** resembles, but is more basic than **ZrO_2**; **ThO_2** is decidedly basic, forming numerous stable salts, and with 1 per cent of ceria constitutes the material of the incandescent gas mantle.

Hydroxides Corresponding with the Typical Oxides

These are precipitated from the corresponding salt solutions by alkali hydroxide; $Ti(OH)_4$ is almost insoluble, and the other hydroxides are quite insoluble in excess of alkali. **Titanium hydroxide,** $Ti(OH)_4$, when precipitated from cold solutions, is readily soluble in acids; **$TiO(OH)_2$**, which is formed from hot solutions, is soluble in acids with much difficulty, and is therefore, probably, polymeric, like β-metastannic acid. A solution of $TiCl_4$ in water probably contains colloidal titanic acid, from which the insoluble form separates on long heating.

Zirconium hydroxides, $ZrO(OH)_2$ and $Zr_3O_4(OH)_4$, resemble those of titanium, except that they are completely insoluble in alkali-hydroxide solution. Alkali zirconates,

formed by fusion, are completely hydrolyzed by water, but the hydroxide tenaciously retains alkali.

Hafnium hydroxide, dried at 100°, is $HfO(OH)_2$.

Thorium hydroxide, $Th(OH)_4$, is a stable, non-acidic, substance, forming ThO_2 directly by ignition.

HALIDES MX_4

The halides show a transition of properties with rise of atomic weight, signifying a change from feebly- to well-developed metallic characters in the elements.

The **fluorides** of the elements of a group often show exceptional properties when compared with the other halides. These properties are, in the case of non-metals, the power to form stable complex acids by combination with hydrofluoric acid, an example of which is seen in hydrofluosilicic acid, H_2SiF_6, and in the case of metals, great differences of solubility, as shown in the case of the alkaline-earth fluorides, when compared with the corresponding chlorides. Both these peculiarities are observable in the fluorides of this sub-group.

Titanium tetrafluoride, TiF_4, is a colourless mass which boils at 284°. Since $TiCl_4$ boils at 136°, TiF_4 is probably polymerized at its boiling-point. The alkali titanifluorides, or hexafluotitanates, $M^{\cdot}_2TiF_6$, are stable salts isomorphous with the corresponding silici-, germani-, and stannifluorides.

Zirconium tetrafluoride, ZrF_4, is sparingly soluble in, and not hydrolyzed by water; $ZrF_4, 3H_2O$ can be crystallized from dilute hydrofluoric acid solution. The zirconifluorides are well-defined salts, isomorphous with the other complex fluorides of the group, whilst the zirconichlorides are not formed in the wet way (cf. titanichlorides).

Hafnium tetrafluoride forms hafnifluorides, or fluohafnates of the types $M^{\cdot}_2HfF_6$ and $M^{\cdot}_3HfF_7$.

Thorium tetrafluoride, ThF_4, is a white, amorphous powder. The hydrate, $ThF_4, 4H_2O$, is formed as a gelatinous precipitate when an alkali fluoride is added to a solution of a thorium salt. Thorifluorides also exist.

Of the **chlorides**, $TiCl_4$ alone is a liquid, boiling at 136°; it is apparently soluble in water, producing probably colloidal suspension of titanic acid. A solution of $TiCl_4$ in hydrochloric acid contains H_2TiCl_6, to which the salt $(NH_4)_2TiCl_6$, $2H_2O$ corresponds. $ZrCl_4$ is crystalline and volatile, and gives with water the oxychloride $ZrOCl_2$; it thus resembles $BiCl_3$ in saline character. $HfCl_4$, like $ZrCl_4$, is volatile, and forms $HfOCl_2$ which is less soluble than $ZrOCl_2$. $ThCl_4$ sublimes when chlorine is passed over a heated mixture of ThO_2 and carbon. It forms crystallohydrates with water and double salts with alkali chlorides.

Oxysalts Corresponding with the Typical Oxides

The existence of **titanic sulphate**, $Ti(SO_4)_2$, is doubtful, but basic sulphates such as $Ti_2O(SO_4)_3$ and $TiOSO_4$ exist, as well as complex titani- and titanylsulphates, e.g. $K_2Ti(SO_4)_4$ and $(NH_4)_2SO_4$, $TiOSO_4$, $4H_2O$. The carbonate and nitrate do not exist, and the sulphide is not formed in the wet way; indeed all titanic salts are completely hydrolyzed by water.

Zirconium sulphate, $Zr(SO_4)_2$, is produced when the hydroxide is dissolved in sulphuric acid. It forms basic salts, and leaves a residue of zirconia on strong ignition. An unstable nitrate exists, and a basic carbonate, but the sulphide is not formed in the wet way.

Hafnium sulphate, $Hf(SO_4)_2$, is rather more stable towards heat than $Zr(SO_4)_2$; the sulphide is formed in the dry way, and several phosphates as well as the oxalate are known.

Thorium sulphate and **nitrate** are well-defined soluble salts which are little hydrolyzed by water. The aqueous solution of the sulphate $Th(SO_4)_2$ forms several crystallohydrates, separating at different temperatures, and also double or complex salts with alkali sulphates. The basic carbonate, obtained by precipitation by alkali-carbonate solution, dissolves in excess of the precipitant, forming a double salt. The sulphide is not formed by precipitation in the wet way.

Derivatives of Lower Oxides

Titanous chloride, $TiCl_3$, is obtained from $TiCl_4$ by reduction with hydrogen. It consists of violet scales which form with water a violet, strongly reducing solution. On this account $TiCl_3$ is used for the volumetric estimation of ferric iron, organic nitro compounds, and other reducible substances.* When heated, this salt decomposes into volatile $TiCl_4$ and non-volatile $TiCl_2$, to which the oxide Ti_2O_2 corresponds. Alkalis precipitate $Ti(OH)_3$; Ti_2O_3, which results from heating TiO_2 in a current of hydrogen, is more basic than the latter oxide, and forms a well-defined **sulphate,** yielding rubidium and cæsium alums. Zirconium forms lower salts, $ZrCl_2$ and possibly $ZrCl_3$; thorium forms none.

Peroxidized Compounds

The peroxides, MO_3, are obtained in a hydrated condition, when aqueous or alcoholic solutions of suitable salts are treated with ammoniacal hydrogen peroxide. The precipitates are peroxy-ortho-acids of the type $M(OOH)(OH)_3$, unless in the case of thorium, which gives Th_2O_7, $4H_2O$.

The titanium compound is yellow, and when potassium fluoride is added to its solution in hydrochloric acid, potassium titanifluoride, K_2TiF_6, is precipitated, and hydrogen peroxide is formed in solution. The hafnium compound is more stable than that of zirconium. Alkali pertitanates and perzirconates of the type, K_4MO_8, $6H_2O$, are known indicating that the peroxy-hydroxides are acidic in character. No perhafnates are known. The thorium compound, Th_2O_7, $4H_2O$, is a basic superoxide which passes by loss of oxygen into the more stable ThO_3.

If hydrogen peroxide be added to an acid solution of zirconium sulphate, a peroxidized basic sulphate, $Zr_2O_6SO_4$, $8H_2O$ is produced, to which no analogy is offered by the other elements.

* *Vide* Knecht and Hibbert's *New Reduction Methods in Volumetric Analysis.*

Titanium gives rise to $(NH_4)_3TiO_2F_5$, ammonium fluoroxypertitanate, which contains the ion $(TiO_2F_5)^{=}$.

Zirconium and hafnium show an extraordinary degree of resemblance attributed to the effect of the lanthanide contraction (q.v.). In consequence, the molecular volumes for example, of the dioxides MO_2, are almost identical; those of the complex fluorides, $(NH_4)_3MF_7$, differ by 1·5 per cent. Methods of separation involving distillation, sublimation, or migration of ions, are unsatisfactory, since they depend more on difference in ionic radii than on particle mass. Nevertheless, hafnium is slightly more basic than zirconium, as is evidenced by the slightly higher decomposition temperature of the sulphate, the higher sublimation temperature (above 200°) of the tetrachloride, and the lower stability of its complex salts.

The crystal structure of the salts, R_2MF_6 is similar to potassium chloroplatinate, K_2PtCl_6, and $(NH_4)_3HfF_7$ has been shown to contain the units $(NH_4)_2HfF_6$ and NH_4F.

CHAPTER IX

GROUP V

SUB-GROUP A		SUB-GROUP B
	7 N (14·01)	
	15 P (31·04)	
23 V (51·0)		33 As (74·96)
41 Cb (93·5)		51 Sb (120·2)
73 Ta (181·5)		83 Bi (208·0)
91 Pa (230·6)		

Nitrogen, the first " typical " element of this group, presents more pronounced acid-producing characters than are met with in any of the preceding groups. For instance, whilst the acids formed by the oxides of carbon and silicon are weak, nitric acid is among the strongest acids.

Diminution of the acidic character of analogous compounds takes place from phosphorus to bismuth in sub-group B; and, in accordance with previously recognized principles, the elements vanadium, columbium, and tantalum, of the A sub-group, are relatively the more base-producing.

SUB-GROUP V B

The ability to form stable, gaseous hydrides is a characteristic of non-metals, and the transition from non-metal to metal in the elements of this group is well shown in the properties of the hydrides, the stability of which diminishes from nitrogen through phosphorus and arsenic to antimony; whilst a hydride of bismuth, though shown to exist, has not been isolated. The heats of formation, which are a measure of relative chemical stability, together with the temperatures of rapid decomposition of these hydrides, are given below:

	Heat of Formation.	Temperature of Rapid Decomposition.
NH_3	118·9 K	1300°
PH_3	36·6 K	440°
AsH_3	−11·7 K	230°
SbH_3	−84·5 K	150°

With the acid-forming properties of the elements themselves are associated base- or salt-forming properties in their hydrides, as is seen by comparing together ammonium and phosphonium compounds. A 0·1 molar solution of ammonia in water contains 1·31 per cent of its ammonia as ionized ammonium hydroxide, it being generally assumed that NH_4OH is formed as a weak base and then ionized; phosphine, however, is only slightly soluble in water, forming a solution which is neutral.

Phosphonium salts, too, are far less stable than those of ammonium; only the halides, and possibly the sulphate, are known, and these are at once decomposed by cold water with

the evolution of phosphine; in the case of ammonium salts an analogous hydrolytic decomposition takes place only slowly on boiling with water. The hydrides of arsenic and antimony do not form salts.

It might be supposed that basic properties of the hydrides would increase from nitrogen to antimony, since the elements themselves become more basigenic. The formation of salts analogous to those of ammonium is, however, simply an extension of the power to produce hydrides, which, in these elements, is a non-metallic property. Increase of electro-positive character in the central atom diminishes the stability of the hydride and, to a greater degree, that of the group MH_4^+. Since, therefore, arsenic, antimony, and bismuth form hydrides of diminishing stability, in conformity with increase of basigenic character, they do not, for the same reason, form the group MH_4^+. As the affinity for hydrogen decreases, so increases the tendency for MCl_3 to co-ordinate negative ions to give $[MCl_4]^-$, where M = As, Sb, or Bi, but not N or P.

Thus the manifestation of basic properties by hydrides, which among all the elements is practically confined to nitrogen, depends upon the possession of non-metallic characteristics by the element, which enable it to take up an ion of hydrogen, forming the radicle, MH_4^+, when it becomes 4-covalent.

The base-forming properties of this class of compound are increased by the exchange of hydrogen atoms for alkyl groups. This is a general rule, which is illustrated likewise by derivatives of sulphur and selenium. Tetra-alkylammonium hydroxides, formed by the action of moist silver oxide on their halides, are analogous in properties to sodium and potassium hydroxides, and possess a strongly alkaline reaction. Tetra-alkylphosphonium salts are much more stable than the simple phosphonium compounds, and they yield the hydroxides by treatment with moist silver oxide. The same is true of tetra-alkylarsonium and stibonium compounds. Bismuth alkyls exist, but they do not possess basic properties.

SUMMARY OF SUB-GROUP V B

Props. of Element.	N	P	As	Sb	Bi
At. Wt.	14·01	31·04	74·96	120·2	208·0
Density	solid {at −195·5 = ·8042; at −252·5 = 1·0265}	Pα 1·83, Pβ 2·10	{Asα 3·88, Asβ 4·71, Asγ 5·73}	Sbβ 5·3, Sbγ 6·7	9 78
M.P.	−214°	Pα 44·1	500° (high pressure)	630°	271°
B.P.	−195·5	290°	—	1440°	1400°
Hydrides	NH_3, N_2H_4, N_2H_2? N_3H	PH_3, P_2H_4, $P_{12}H_6$, P_9H_2	AsH_3, As_2H_2	SbH_3	—
Oxides X_2O ..	N_2O	—	As_2O?	—	—
X_2O_2	NO	—	—	—	Bi_2O_2?
X_2O_3	{$N_4O_6 \rightleftharpoons 2N_2O_3 \rightleftharpoons 2NO + 2NO_2$}	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
X_2O_4	$N_2O_4 \rightleftharpoons 2NO_2$	P_2O_4	As_2O_4?	Sb_2O_4	Bi_2O_4
X_2O_5	N_2O_5	P_4O_{10}	As_4O_5	Sb_2O_5	Bi_2O_5
Hydroxides $X_2(OH)_2$	$N_2(OH)_2$	[H_2POOH]			
{$XO{\cdot}OH$, $X_2O(OH)_4$	$NO{\cdot}OH$	$PO{\cdot}OH$	{$AsO{\cdot}ONa$*, $As_2O{\cdot}(ONa)_4$}	{$SbO{\cdot}ONa$, $Sb_2O{\cdot}(OH)_4$}	—
{$X(OH)_3$	—	$P(OH)_3 \rightleftharpoons HPO(OH)_2$	$As(OAg)_3$	$Sb(OH)_3$	$Bi(OH)_3$
{$X_2O_2(OH)_4$ ..	—	$P_2O_2(OH)_4$	—	—	—
{$X_2O_3(OH)_2$ ..	—	—	—	$Sb_2O_3(ONa)_2$	—
{$XO_2{\cdot}OH$	$NO_2{\cdot}OH$	$PO_2{\cdot}OH$	$AsO_2{\cdot}OH$	$SbO_2{\cdot}OH$	$BiO_2{\cdot}OH$
{$X_2O_3(OH)_4$ ..	—	$P_2O_3(OH)_4$	$As_2O_3(OH)_4$	$Sb_2O_3(OH)_4$	—
{$XO(OH)_3$	—	$PO(OH)_3$	$AsO(OH)_3$	$SbO(OH)_3$	—
{$X(OH)_5$	—	—	—	—	—
Chlorides—					
XCl_2	—	—	—	—	$BiCl_2$
XCl_3, $XOCl$ ..	NCl_3, $NOCl$	PCl_3	$AsCl_3$, $AsOCl$, $As(OH)_2Cl$	$SbCl_3$, $SbOCl$	$BiCl_3$, $BiOCl$
XCl_5, $XOCl_3$ ..	—	PCl_5, $POCl_3$	—	$SbCl_5$	—

* Where the acid itself is unknown the sodium or other salt is given.

Passing from the B to the A sub-group, it is found that none of the elements of the latter group form gaseous hydrides. This is consistent with what has previously been observed, namely, that members of sub-groups A form neither volatile hydrides nor volatile organo-metallic compounds.

By reference to the synoptic table on the previous page, it will be seen that numerous oxygen compounds are known belonging to a number of different types. In a general study of the oxides or hydroxides of any group two considerations must be borne in mind: (i) the diminution of acid-forming properties with increasing atomic weight, these persisting longer in the B than in the A sub-groups; (ii) the enhancing of these properties in a particular element by the addition of oxygen. Thus, for example, (i) taking the type R_2O_5 the acidic properties diminish in the series N_2O_5, P_2O_5, As_2O_5, Sb_2O_5, Bi_2O_5 from member to member, and (ii) considering the series $NH_4OH \rightarrow N(OH)_5$, the latter of which is represented in a meta form by $NO_2 \cdot OH$, the properties of the compounds change from those of a weak base to those of a powerful acid.

Inasmuch as nitrogen and phosphorus possess strong individuality and form some types of compounds which are unrepresented among the other members of the group, it will be convenient to study them separately. Arsenic, antimony, and bismuth will then be compared with one another and with phosphorus, and finally the members of the A sub-group will be briefly considered.

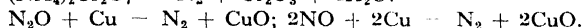
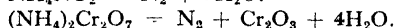
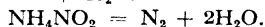
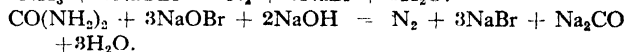
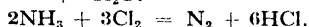
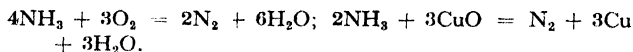
NITROGEN

The atmosphere is the chief storehouse of nitrogen; thus the greater part of this element on our planet exists in the free state. This fact may be attributed to the inertness of nitrogen; that is, the difficulty with which it combines with other elements.

The subject of the fixation and circulation of nitrogen will

be dealt with at the end of this chapter; here it may be noted that the methods for preparing nitrogen artificially consist either in the oxidation of ammonia and its derivatives, or in the reduction of oxides of nitrogen.

This is shown in the following reactions:

$4NH_3 + 3O_2 = 2N_2 + 6H_2O$; $2NH_3 + 3CuO = N_2 + 3Cu + 3H_2O$.
$2NH_3 + 3Cl_2 = N_2 + 6HCl$.
$2NH_3 + 3NaOBr = N_2 + 3NaBr + 3H_2O$.
$CO(NH_2)_2 + 3NaOBr + 2NaOH = N_2 + 3NaBr + Na_2CO + 3H_2O$.
$NH_4NO_2 = N_2 + 2H_2O$.
$(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4H_2O$.
$N_2O + Cu = N_2 + CuO$; $2NO + 2Cu = N_2 + 2CuO$.

Active Nitrogen.—When nitrogen passing through a tube at low pressure is submitted to a high-tension electric discharge, the gas glows and is converted into an active, probably atomic, form * of the gas which transforms white into red phosphorus, forms nitrides with sodium and mercury at 150°, and combines with NO to form $NO_2 + N_2$, and acetylene to form HCN.

Hydrides of Nitrogen

Nitrogen forms the following compounds with hydrogen:

NH_3 Ammonia,
N_2H_4 Hydrazine or Diamide,
N_2H_2 Di-imide (existence doubtful),
N_3H Hydrazoic acid or Azoimide.

This series of compounds shows a transition from basic to acidic properties, with a decrease in the proportion of hydrogen. N_3H is more acidic than SH_2, and is comparable with the hydracids of the seventh group, the complex N_3 being analogous to a halogen atom. Increase in acidity with loss of hydrogen is a general phenomenon well illustrated in certain carbon compounds, for instance, the series:

$$C_2H_6,\ C_2H_4,\ C_2H_2;$$

* Strutt, *Chem. Soc. Trans.* (1918); **113**, 200

the last only of these compounds, acetylene, behaving as an acid, its hydrogen atoms being replaceable by metals.

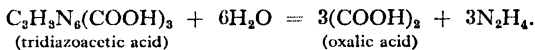
Ammonia, NH_3.—Of this substance little need be said, its methods of preparation and properties being well known.

One or more of the hydrogen atoms of NH_3 may be replaced by different elements or radicles, the nature of the resulting compound depending on the properties of the substituting atom or group. The alkali metals produce compounds of the type NH_2M, e.g. sodamide, NH_2Na, which on contact with water breaks up into ammonia and sodium hydroxide. Sodium hypochlorite yields **chloramine,** NH_2Cl, an unstable oil giving with alkalis NH_3 and N_2. Hydrocarbon radicles may replace one, two, or three atoms of hydrogen, producing respectively primary, secondary, and tertiary amines. The aliphatic amines are more basic than ammonia, the basic properties increasing with successive replacement of hydrogen atoms, as in the series NH_3; $NH_2C_2H_5$; $NH(C_2H_5)_2$; $N(C_2H_5)_3$. The aromatic amines are less basic than ammonia, and their basic properties diminish with successive replacement, as in the series NH_3; $NH_2C_6H_5$; $NH(C_6H_5)_2$; $N(C_6H_5)_3$. Triphenylamine, $N(C_6H_5)_3$, is not a base.

Ammonia reacts with acid chlorides to produce amides, $RCONH_2$, which are either neutral substances or possess very feebly basic or acidic properties.

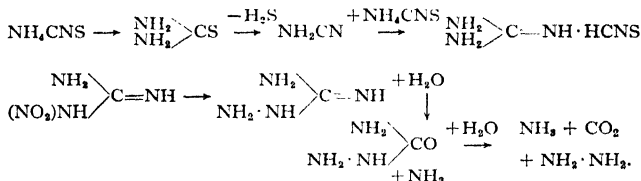
Acetamide, $CH_3 \cdot CO \cdot NH_2$, shows feebly basic properties by forming an unstable salt, $CH_3 \cdot CO \cdot NH_3Cl$, with hydrochloric acid; and feebly acidic properties by dissolving mercuric oxide to form $(CH_3 \cdot CO \cdot NH)_2Hg$.

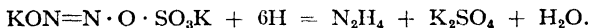
Hydrazine or Diamide, $N_2H_4(= H_2N - NH_2)$, was obtained by Curtius in 1887 by the hydrolysis of tridiazoacetic acid by dilute mineral acids:

$$\underset{\text{(tridiazoacetic acid)}}{C_3H_3N_6(COOH)_3} + 6H_2O = \underset{\text{(oxalic acid)}}{3(COOH)_2} + 3N_2H_4.$$

Hydrazine is prepared by the prolonged heating of ammonium

thiocyanate, and nitration of the guanidine thus formed. The nitroguanidine is then reduced in acid solution, and a hydrazine salt obtained after elimination of the carbon dioxide formed as a by-product. The following changes occur:

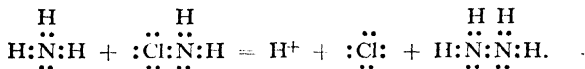
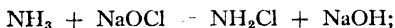
$$NH_4CNS \longrightarrow \genfrac{}{}{0pt}{}{NH_2}{NH_2}\!\!>\!CS \xrightarrow{-H_2S} NH_2CN \xrightarrow{+NH_4CNS} \genfrac{}{}{0pt}{}{NH_2}{NH_2}\!\!>\!C{=}NH \cdot HCNS$$

$$\genfrac{}{}{0pt}{}{NH_2}{(NO_2)NH}\!\!>\!C{=}NH \longrightarrow \genfrac{}{}{0pt}{}{NH_2}{NH_2 \cdot NH}\!\!>\!C{=}NH \xrightarrow{+H_2O} \genfrac{}{}{0pt}{}{NH_2}{NH_2 \cdot NH}\!\!>\!CO + NH_3 \xrightarrow{+H_2O} NH_3 + CO_2 + NH_2 \cdot NH_2.$$

Hydrazine is also formed from an inorganic source when potassium nitrososulphate, formed by the union of nitric oxide with potassium sulphite, is reduced in aqueous solution by sodium amalgam. The reaction is probably:

$$KON{=}N \cdot O \cdot SO_3K + 6H = N_2H_4 + K_2SO_4 + H_2O.$$

Further reduction by the amalgam produces ammonia.

Hydrazine is best prepared by the oxidation of ammonia in solution by sodium hypochlorite in presence of a little glue which acts as a protective colloid, inhibiting the reaction: $2NH_2Cl + N_2H_4 = 2NH_4Cl + N_2$. The reaction is in two parts, monochloramine being an intermediate product, thus:

$$NH_3 + NaOCl = NH_2Cl + NaOH;$$

$$\mathrm{H{:}\overset{H}{\underset{\cdot\cdot}{\ddot{N}}}{:}H} + \mathrm{{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}\overset{H}{\underset{\cdot\cdot}{\ddot{N}}}{:}H} = H^+ + \mathrm{{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}} + \mathrm{H{:}\overset{H}{\underset{\cdot\cdot}{\ddot{N}}}{:}\overset{H}{\underset{\cdot\cdot}{\ddot{N}}}{:}H}.$$

It is crystallized from the solution as hydrazine sulphate.

An aqueous solution of hydrazine, prepared by distilling a salt with alkali, is alkaline, and probably contains the dihydrate, $HONH_3{-}NH_3OH$. The monohydrate is obtained on evaporation as a highly refractive liquid, slightly heavier than water, boiling at 118·5°, and remaining liquid at −40°. It is hydrazonium hydroxide, $NH_2{-}NH_3(OH)$.

Pure hydrazine was obtained by Lobry de Bruyn by treatment of the hydrate with anhydrous baryta and distillation under reduced pressure, as a hygroscopic liquid, boiling at 113·5° under ordinary pressure, and solidifying at 1·4°. It reacts vigorously with water, forming the monohydrate, and decomposes when heated thus: $3N_2H_4 = N_2 + 4NH_3$.

Hydrazine is a powerful reducing agent, precipitating silver, mercury, and gold from their solutions at atmospheric temperature. Fehling's solution also is easily reduced. The reaction is essentially $N_2H_4 + 2O = N_2 + 2H_2O$, nitrogen being evolved. Azoimide, N_3H, results from the oxidation of hydrazine by hydrogen peroxide and sulphuric acid.

Hydrazine forms two hydrochlorides, N_2H_4, HCl and N_2H_4, 2HCl; both salts are easily soluble in water.

The dihydrochloride melts at 198°, losing HCl, and forming the monohydrochloride, which melts at 89°.

The sulphate, N_2H_4, H_2SO_4, is sparingly soluble in water.

Although hydrazine has only comparatively recently been isolated, its substitution compounds, particularly phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, were known previously. The formation of hydrazides, $R \cdot CO \cdot NH \cdot NH_2$, and hydrazones, $R_2C : N \cdot NH_2$, by hydrazine and its derivatives, are valuable reactions in the study of the carbon compounds.

Hydrazoic Acid or **Azoimide,** N_3H.

The following substances may contain the azo grouping, —N=N—:

Hyponitrous acid HO · N=N · OH

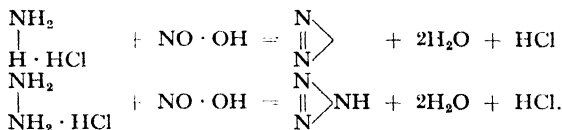
Azoimide $\begin{array}{c} N{=}N \\ \diagdown\diagup \\ NH. \end{array}$

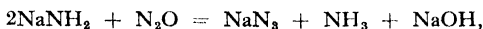
Nitrous oxide N=N=O or N=O=N.

Di-imide, HN = NH, belongs to the same category, but has never been isolated. Azoimide was first obtained by Curtius from hippuryl hydrazine ($C_6H_5CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$) and nitrous acid, the hippurylazoimide produced being hydrolyzed by dilute acid or alkali.

Azoimide may be obtained by the action of nitrous acid on salts of hydrazine. This method of preparation is analogous to that by which nitrogen is obtained from ammonium salts:

$$\begin{array}{l} NH_2 \\ | \\ H \cdot HCl \end{array} + NO \cdot OH = \begin{array}{l} N \\ \| \\ N \end{array} \rangle + 2H_2O + HCl$$

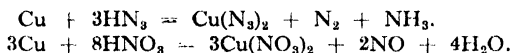
$$\begin{array}{l} NH_2 \\ | \\ NH_2 \cdot HCl \end{array} + NO \cdot OH = \begin{array}{l} N \\ \| \\ N \end{array} \rangle NH + 2H_2O + HCl.$$

W. Wislicenus prepared azoimide by the interaction of nitrous oxide and sodamide thus:

$$2NaNH_2 + N_2O = NaN_3 + NH_3 + NaOH,$$

the sodium salt being decomposed by sulphuric acid and the acid obtained by distillation.

Pure azoimide, obtained by distilling the potassium salt with dilute sulphuric acid, and condensing the dried vapours by means of liquid air, is a mobile liquid with a penetrating smell, boiling at 37°, freezing at −80°, and highly explosive. A dilute aqueous solution has an acid reaction, having undergone electrolytic dissociation to the extent of about 1 per cent. This substance is therefore known as **hydrazoic acid**, and its salts as hydrazoates or azides. The silver, mercurous, and lead salts are sparingly soluble in water, thus resembling the corresponding halides. Like the acid itself, they are explosive.

The soluble alkali azides decompose at 300° evolving nitrogen. The red colour due to ferric azide forms a convenient test for the acid.

According to E. C. Franklin (1934), magnesium alone liberates hydrogen in small amount from hydrazoic acid; metals such as zinc, iron, manganese, or copper, produce the corresponding azides, nitrogen, and ammonia. The acid oxidizes ferrous azide to the ferric salt. Its analogy to nitric acid is apparent, and Franklin considers it to be ammononitric acid.

$$Cu + 3HN_3 = Cu(N_3)_2 + N_2 + NH_3.$$
$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

As an alternative to the ring formula given above for the acid, Thiele suggested the structure $N{\equiv}N{=}NH$, since by its reduction, NH_3 and N_2H_4 are produced. Since quinquivalent nitrogen is inadmissable, this must be represented as $H{-}N{=}N{\rightarrow}N$. The parachors and small dipole moments of the organic azides indicate that resonating structures are present therein, $R{-}N{=}N{\rightarrow}N$ and $R{-}N{\leftarrow}N{\equiv}N$. The ion, N_3^-, is undoubtedly linear, as shown by X-ray analysis and by the similarity of properties between NaN_3 and NaNCO. (Cranston and Livingstone, *J. Chem. Soc.* (1926), 501.)

The relation between nitrous oxide and the azide and cyanate ions may be shown electronically thus:

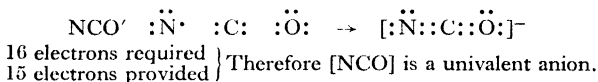
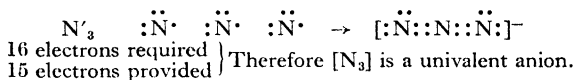
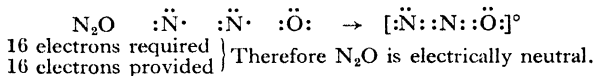
$$N_2O \quad :\ddot{N}\cdot \quad :\ddot{N}\cdot \quad :\ddot{O}: \quad \rightarrow \quad [:\ddot{N}::N::\ddot{O}:]^{\circ}$$

16 electrons required } Therefore N_2O is electrically neutral.
16 electrons provided }

$$N'_3 \quad :\ddot{N}\cdot \quad :\ddot{N}\cdot \quad :\ddot{N}\cdot \quad \rightarrow \quad [:\ddot{N}::N::\ddot{N}:]^-$$

16 electrons required } Therefore $[N_3]$ is a univalent anion.
15 electrons provided }

$$NCO' \quad :\ddot{N}\cdot \quad :C: \quad :\ddot{O}: \quad \rightarrow \quad [:\ddot{N}::C::\ddot{O}:]^-$$

16 electrons required } Therefore [NCO] is a univalent anion.
15 electrons provided }

From band spectrum measurements it is concluded that nitrous oxide has a linear molecule, though the order of attachment of the atoms is still uncertain.

Such molecules or ions showing identity of outer electronic configurations are called *isosteres*. It is not surprising that the ions N_3^- and NCO^- form isomorphous alkali salts, or that $O{=}C{=}O$, isosteric with $N{=}N{=}O$, should possess similar physical properties. Chemical properties, however, will differ.

Classification of Certain Nitrogen Compounds

The various classes of compounds each of which contains a single nitrogen atom may be advantageously summarized according to the following scheme, which shows the various stages of oxidation:

NX_3

NH_3 base
NH_2OH base
$NH \cdot (OH)_2$ dihydroxyammonia
Dehydration products
$(N \cdot OH)_2$, hyponitrous acid, and N_2O
[$N(OH)_3$] orthonitrous acid
$NO \cdot OH$ (meta)nitrous acid
N_2O_3 anhydride

NX_5

[NH_5]NH_4Cl
NH_4OH
[$NH_3(OH)_2$]
Dehydration product ONR_3 (oxyamines)
[$NH_2(OH)_3$]
[$NH(OH)_4$]
Dehydration product $R—NO_2$ (nitro-compounds)
[$N(OH)_5$] orthonitric acid HNO_3, $2H_2O$
[$NO(OH)_3$] mesonitric acid HNO_3, H_2O
$NO_2 \cdot OH$ (meta)nitric acid
N_2O_5 anhydride

Compounds in square brackets are unknown.

NX_3 Type

Hydroxylamine, $NH_2 \cdot OH$(oxyammonia), was discovered in 1865 by Lossen, who obtained it by the action of nascent hydrogen on nitric oxide:

$$2NO + 6H = 2NH_2 \cdot OH.$$

It is also formed by the reduction of nitric acid by tin or zinc, and may be produced and identified by the following simple experiment:

"Pour some dilute sulphuric acid on zinc, and then a little nitric acid, when the effervescence will lessen to a marked extent; in half a minute pour off the acid solution and add potash in large excess to dissolve the zinc hydroxide; then add a little very dilute copper-sulphate solution. A yellow precipitate of hydrated cuprous oxide will be produced." * This reaction may be represented by the following equation:

$$HNO_3 + 6H = NH_2 \cdot OH + 2H_2O.$$

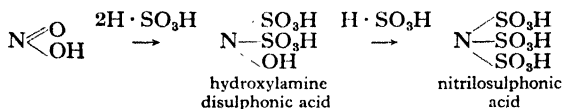
Hydroxylamine may also be obtained by the reduction of nitroparaffins, such as $CH_3 \cdot NO_2$, or of ethylnitrate, $C_2H_5NO_3$,

* Divers.

but the most important method for the production of this substance consists in the sulphonation of nitrous acid by sulphurous acid and the hydrolytic reduction of the product.

The following scheme represents the mechanism of the sulphonation of nitrous acid:

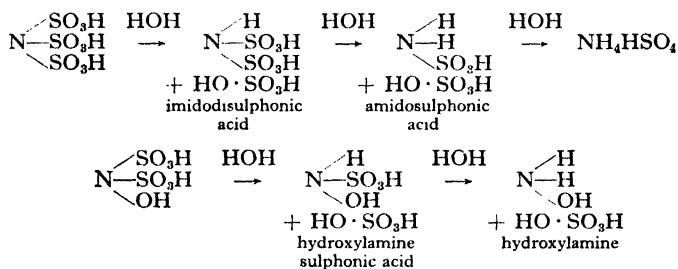
$$N{\lt}^{O}_{OH} \xrightarrow{2H\cdot SO_3H} N\begin{cases} SO_3H \\ SO_3H \\ OH \end{cases} \xrightarrow{H\cdot SO_3H} N\begin{cases} SO_3H \\ SO_3H \\ SO_3H \end{cases}$$

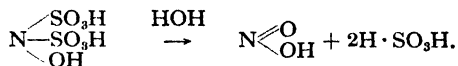
hydroxylamine disulphonic acid — nitrilosulphonic acid

The hydrolysis of these two products may be effected in two ways. If water or dilute acid is used there is reduction with simultaneous production of sulphuric acid:

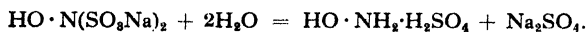
$$N\begin{cases} SO_3H \\ SO_3H \\ SO_3H \end{cases} \xrightarrow{HOH} N\begin{cases} H \\ SO_3H \\ SO_3H \end{cases} + HO\cdot SO_3H \xrightarrow{HOH} N\begin{cases} H \\ H \\ SO_3H \end{cases} + HO\cdot SO_3H \xrightarrow{HOH} NH_4HSO_4$$

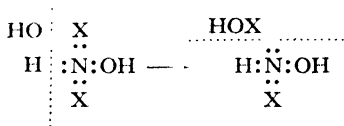
imidodisulphonic acid — amidosulphonic acid

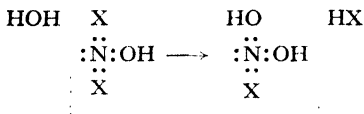
$$N\begin{cases} SO_3H \\ SO_3H \\ OH \end{cases} \xrightarrow{HOH} N\begin{cases} H \\ SO_3H \\ OH \end{cases} + HO\cdot SO_3H \xrightarrow{HOH} N\begin{cases} H \\ H \\ OH \end{cases} + HO\cdot SO_3H$$

hydroxylamine sulphonic acid — hydroxylamine

Hydrolysis by alkalis does not involve reduction, and sulphite is regenerated:

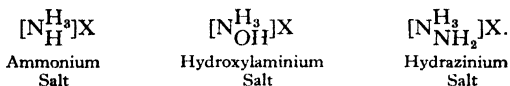
$$N\begin{cases} SO_3H \\ SO_3H \\ OH \end{cases} \xrightarrow{HOH} N{\lt}^{O}_{OH} + 2H\cdot SO_3H.$$

According to Divers, normal sulphites do not react with alkali nitrites. Nitrous and sulphurous acids react, but the presence of a base is necessary to combine with the products and render them stable. Thus the alkali salts of hydroxylamine disulphonic and nitrilosulphonic acids may be obtained, and when the former are boiled with dilute acids, salts of hydroxylamine are produced:

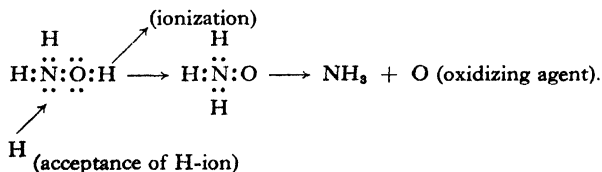
$$HO\cdot N(SO_3Na)_2 + 2H_2O = HO\cdot NH_2\cdot H_2SO_4 + Na_2SO_4.$$

How the hydrolysis of the compound NX_2OH (where X is SO_3H) proceeds depends upon the kind of approach made by the attacking water molecules, or rather whether hydrions or hydroxidions predominate in the solution. The two ways of approach are seen in the following schemes, in which only essential electrons are shown:

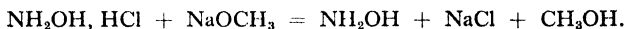
$$
\begin{array}{lcl}
\mathrm{HO}\;\vdots\;\;\mathrm{X} & & \mathrm{HOX} \\
\mathrm{H}\;\vdots\;:\ddot{\underset{..}{\mathrm{N}}}:\mathrm{OH} & \longrightarrow & \mathrm{H}:\ddot{\underset{..}{\mathrm{N}}}:\mathrm{OH} \\
\quad\;\vdots\;\;\mathrm{X} & & \quad\;\mathrm{X}
\end{array}
$$

In acid solution hydrion attaches itself to the lone pair of electrons of the nitrogen atom, and X combines with hydroxidion.

$$
\begin{array}{lcll}
\mathrm{HOH}\;\;\mathrm{X} & & \mathrm{HO} & \mathrm{HX} \\
\quad\;:\ddot{\underset{..}{\mathrm{N}}}:\mathrm{OH} & \longrightarrow & :\ddot{\underset{..}{\mathrm{N}}}:\mathrm{OH} & \\
\qquad\;\mathrm{X} & & \;\;\mathrm{X} &
\end{array}
$$

In alkaline solution hydroxidion displaces X from combination with the nitrogen atom.

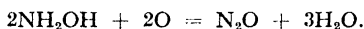
To anticipate somewhat, it may be noted that salts of hydroxylamine, NH_2OH, HX, contain the basic radicle $[NH_3OH]$, so that the following analogy holds:

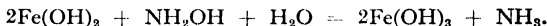
$[\mathrm{N}^{\mathrm{H_3}}_{\mathrm{H}}]\mathrm{X}$	$[\mathrm{N}^{\mathrm{H_3}}_{\mathrm{OH}}]\mathrm{X}$	$[\mathrm{N}^{\mathrm{H_3}}_{\mathrm{NH_2}}]\mathrm{X}$.
Ammonium Salt	Hydroxylaminium Salt	Hydrazinium Salt

The behaviour of hydroxylamine either as a base, an acid, or an oxidizing agent is shown in the following scheme:

$$
\begin{array}{c}
\mathrm{H} \qquad\qquad \nearrow^{\text{(ionization)}} \quad \mathrm{H} \\
\mathrm{H}:\ddot{\underset{..}{\mathrm{N}}}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H} \longrightarrow \mathrm{H}:\ddot{\underset{..}{\mathrm{N}}}:\mathrm{O} \longrightarrow \mathrm{NH_3} + \mathrm{O}\ \text{(oxidizing agent).} \\
\nearrow \qquad\qquad\qquad \mathrm{H} \\
\mathrm{H}\ \text{(acceptance of H-ion)}
\end{array}
$$

Pure anhydrous hydroxylamine was prepared in 1891 by Lobry de Bruyn, by bringing together hydroxylamine hydrochloride and sodium methoxide in methyl-alcoholic solution, sodium chloride being precipitated:

$$NH_2OH, HCl + NaOCH_3 = NH_2OH + NaCl + CH_3OH.$$

The hydroxylamine was fractionated under reduced pressure, after distilling off the methyl alcohol, and obtained as a white crystalline solid, melting at 33° and boiling at 58° under 22 mm. pressure. Crismer obtained it in the same year by distilling $ZnCl_2, 2NH_2OH$.

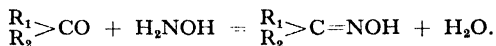
An aqueous solution of hydroxylamine is alkaline, but unstable, soon breaking up into nitrogen, ammonia, and water according to the reaction: $3NH_2OH = N_2 + NH_3 + 3H_2O$. It reduces copper, mercury, silver, and gold solutions, and decolorizes iodine with evolution of nitrous oxide thus:

$$2NH_2OH + 2O = N_2O + 3H_2O.$$

In presence of alkali, however, ferrous iron is oxidized thus:

$$2Fe(OH)_2 + NH_2OH + H_2O = 2Fe(OH)_3 + NH_3.$$

Hydroxylamine reacts with nitrous acid, first producing hyponitrous acid and then nitrous oxide:

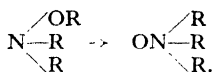
$$\begin{aligned} NH_2OH + HONO &= HON{=}NOH + H_2O \\ HON{=}NOH &= N_2O + H_2O. \end{aligned}$$

Hydroxylamine is employed for the preparation of oximes, which are formed from aldehydes and ketones according to the reaction:

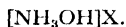
$$\begin{matrix}R_1\\R_2\end{matrix}{>}CO + H_2NOH = \begin{matrix}R_1\\R_2\end{matrix}{>}C{=}NOH + H_2O.$$

It is chiefly known in the form of its crystalline salts, such as the hydrochloride, sulphate, and nitrate, which are more stable than the free base.

Mono- and di- substituted hydroxylamines, $NHR_1 \cdot OH$ and

$NR_1R_2 \cdot OH$ exist, but the displacement of the third hydrogen atom results in the formation of an oxyamine,* thus:

$$N\begin{cases}OR\\R\\R\end{cases} \rightarrow ON\begin{cases}R\\R\\R.\end{cases}$$

Oxyamines, which are bases, may likewise be obtained by the action of hydrogen peroxide on tri-substituted amines, NR_3.

Ebler and Schott † believe hydroxylamine itself to be tautomeric, thus: $NH_2-OH \rightleftharpoons NH_3O$. They regard the form NH_2OH as feebly acidic, since calcium displaces hydrogen from hydroxylamine, forming the compound $Ca(ONH_2)_2$, calcium hydroxylamate. NH_3O would thus be the basic form, while the hydroxylamine salts become oxonium compounds,

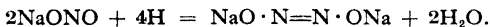
$$[NH_3OH]X.$$

Hyponitrous acid, $H_2N_2O_2$, stands midway, as regards stage of oxidation, between hydroxylamine and nitrous acid. The basic properties which characterize ammonia, and are less pronounced in hydroxylamine, give place to feebly acidic properties in hyponitrous acid, which is comparable in strength with carbonic acid. Acidic properties are further increased in nitrous acid.

On consideration of the relationship of hyponitrous acid to hydroxylamine and to nitrous acid, the following methods of preparation may be proposed:

(*a*) Reduction of nitrous acid.
(*b*) Oxidation of hydroxylamine.
(*c*) Combination of nitrous acid with hydroxylamine.

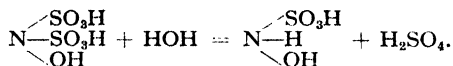
Each of these methods can be realized.

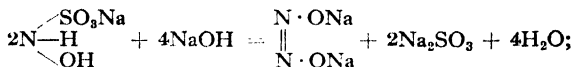
(*a*) Sodium hyponitrite is formed by the action of sodium amalgam on sodium nitrite solution:

$$2NaONO + 4H = NaO \cdot N{=}N \cdot ONa + 2H_2O.$$

Again, as was previously shown, hydroxylamine sulphonic

* Dunstan and Goulding, *Chem. Soc. Trans.* (1899), **75**, 1004.
† *J. pr. Chem.* (1908), ii, **78**, 289.

acid is formed by the hydrolytic reduction of hydroxylamine disulphonic acid, obtained by the sulphonation of nitrous acid:

$$N\begin{matrix}\diagup SO_3H \\ -SO_3H \\ \diagdown OH\end{matrix} + HOH = N\begin{matrix}\diagup SO_3H \\ -H \\ \diagdown OH\end{matrix} + H_2SO_4.$$

If the alkali salt of this acid is hydrolyzed by fusion with caustic alkali, which does not involve reduction, hyponitrite is produced:

$$2N\begin{matrix}\diagup SO_3Na \\ -H \\ \diagdown OH\end{matrix} + 4NaOH = \begin{matrix}N \cdot ONa \\ \| \\ N \cdot ONa\end{matrix} + 2Na_2SO_3 + 4H_2O;$$

thus, indirectly, nitrous is reduced to hyponitrous acid.

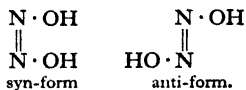
(*b*) Hyponitrous acid also results from the oxidation of hydroxylamine by sodium hypobromite or silver oxide.

(*c*) The same acid may also be prepared by introducing nitrous anhydride into a methyl alcoholic solution of hydroxylamine:

$$2NH_2OH + N_2O_3 = 2H_2N_2O_2 + H_2O.$$

Silver hyponitrite is formed as a yellow precipitate when silver nitrate is added to a solution of the alkali salt; and thence the acid itself can be isolated by the use of ethereal hydrochloric acid. On evaporation of the ether the acid remains as a white, crystalline solid, which dissolves in cold water; but its solution decomposes on warming, with evolution of nitrous oxide.

The molecular weight of hyponitrous acid, determined by the cryoscopic method, corresponds with the formula $H_2N_2O_2$. Acid and normal salts exist, e.g. KHN_2O_2 and $K_2N_2O_2$. These facts, together with its modes of formation, indicate that hyponitrous acid is diazodihydroxide. It is possible, in accordance with the Hantzsch-Werner view of the stereochemistry of nitrogen, that such a substance may exist in two stereoisomeric forms, known respectively as syn- and anti- forms:

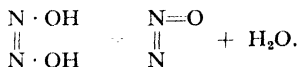
$$\underset{\text{syn-form}}{\begin{matrix}N \cdot OH \\ \| \\ N \cdot OH\end{matrix}} \qquad \underset{\text{anti-form.}}{\begin{matrix}N \cdot OH \\ \| \\ HO \cdot N\end{matrix}}$$

If two such bodies did exist, the syn-form should yield nitrous oxide and water more easily than the anti-form, owing to the closer proximity of the hydroxyl groups.

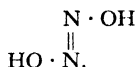
An isomer of hyponitrous acid exists in nitramide, the amide of nitric acid. This substance is obtained by acidic hydrolysis of salts of nitrocarbamic acid:

$$CO\langle{}^{OK}_{NH \cdot NO_2} + H_2O = CO\langle{}^{OK}_{OH} + NH_2 \cdot NO_2.$$

Nitramide crystallizes in white leaflets, which melt at 72° to 75° with rapid decomposition. Its aqueous solution is strongly acid; and its salts easily decompose in solution, giving off nitrous oxide.

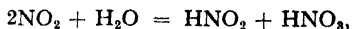
These facts do not accord with the idea that the substance is the amide of nitric acid. There are two views as to its constitution. Thiele believed it to be imidonitric acid, $HN{=}N\langle{}^{\mathrm{O}}_{\mathrm{OH}}$, both hydrogen atoms being replaceable by metals. Hantzsch is of opinion that this substance is syndiazohydroxide, owing to the great ease with which it yields nitrous oxide by decomposition when heated:

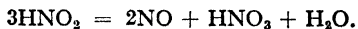
$$\begin{array}{l} N \cdot OH \\ \| \\ N \cdot OH \end{array} = \begin{array}{l} N{=}O \\ \| \\ N \end{array} + H_2O.$$

Under these circumstances hyponitrous acid would be antidiazohydroxide:

$$\begin{array}{r} N \cdot OH \\ \| \\ HO \cdot N. \end{array}$$

Nitrous acid, the final oxidation product of ammonia, is more unstable than hyponitrous acid, for, unlike the latter substance, it cannot be obtained pure. The ortho-form, $N(OH)_3$, is unknown, although Na_3NO_3 exists. The ordinary nitrites are meta-salts, $NO \cdot OM$, and are very stable, but when the acid is liberated in solution it decomposes thus:

$$4HNO_2 = 2NO + 2NO_2 + 2H_2O;$$

but NO_2 reacts with water thus:

$$2NO_2 + H_2O = HNO_2 + HNO_3,$$

so that, unless the solution is concentrated, no brown NO_2 leaves it, and the result, expressed by the sum of these equations, is:

$$3HNO_2 = 2NO + HNO_3 + H_2O.$$

A solution of nitrous acid, obtained by dissolving its anhydride in water at low temperature, undergoes the same change on warming.

When silver nitrite reacts with an alkyl iodide a nitro-paraffin, or a mixture of nitroparaffin with alkyl nitrite, is produced. Methyl iodide gives nitromethane, $CH_3{\cdot}NO_2$, only, ethyl iodide yields a mixture of nitroethane, $C_2H_5{\cdot}NO_2$, and ethyl nitrite, $C_2H_5{\cdot}O{\cdot}NO$; and the proportion of nitro-derivative diminishes with rise in the homologous series. From this it may be concluded either that silver nitrite can exist in the two forms $Ag{\cdot}O{\cdot}NO$ and $Ag{\cdot}NO_2$, or, if in the first form only, that alkyl nitrites undergo partial or complete transformation into nitroparaffins. Since the proportion between the amount of nitrite and nitro-compound formed varies when different alkyl compounds are used, it seems reasonable to assume that the phenomenon depends on the alkyl compound rather than on the structure of silver nitrite. Now, according to recent views of molecular structure, metallic nitrites are ionized in the solid state, and therefore do not exist in two molecular forms. If this is the case with silver nitrite, then it is the nitrite ion, whose structure is [O—N=O], which reacts with the alkyl group, and whether a nitrite or a nitro-compound is formed must depend upon the behaviour of the particular alkyl group towards this ion.

Nevertheless, nitrites of some of the feebler metals are pale yellow, like organic nitro-compounds. Silver nitrite in large crystals is slightly yellow, and so is mercurous nitrite. It may

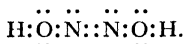
be, therefore, that non-ionized metallic nitrites can have a nitro-constitution.

Nitrites are prepared from nitrates by removal of oxygen, e.g.: $NaNO_3 + Pb = NaNO_2 + PbO$; they are soluble in, unless decomposed by, water; silver nitrite crystallizes readily from hot water. There are many double or complex nitrites e.g. $CsAg(NO_2)_2$, $K_2Pb(NO_2)_4$, $K_3Co(NO_2)_6$.

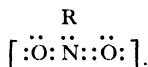
STRUCTURE OF HYPONITROUS AND NITROUS ACIDS

The formulation, given before, of hyponitrous acid as symmetrical anti-diazohydroxide, is confirmed by the zero dipole moment of its esters. There seems little doubt that its formula is $(HNO)_2$, for, while nitric oxide and atomic hydrogen at low temperature produce hyponitrous acid, nitric oxide and sodium, in liquid ammonia solution yield sodium nitrosyl, $(NaNO)_n$, which is distinguished from sodium hyponitrite by its different X-ray diagram and by yielding NO and not N_2O with acids. This is comparable with NaCO, sodium carbonyl, which is prepared in analogous fashion from CO.

Hyponitrous acid is thus:

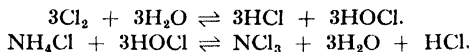
$$\mathrm{H:\ddot{\underset{\cdot\cdot}{O}}:\ddot{N}::\ddot{N}:\ddot{\underset{\cdot\cdot}{O}}:H.}$$

The nitrite ion $[O{-}N{=}O]^-$ is represented electronically thus: $[:\ddot{\underset{\cdot\cdot}{O}}:\ddot{N}::\ddot{O}:]$. It is seen to be a univalent anion because it contains 18 electrons, only 17 of which are provided by its constituent atoms. It appears that the nitro-group $[O{=}\overset{|}{N}{=}O]$ containing quinquivalent nitrogen cannot exist, for if the N atom were bound to each of two oxygen atoms with a double bond, the union of that atom with another atom would be impossible, since all its eight electrons would be engaged, thus $[:\ddot{O}::N::\ddot{O}:]$. Moreover, if such a combination were formed it would be a univalent cation, since it would contain only 16 electrons, although its constituent atoms possessed between them, when free, 17

electrons. It follows therefore that the NO_2 group is always $[:\underset{\cdot\cdot}{\ddot{O}}:\ddot{N}::\ddot{O}:]$—whether nitrite or nitro—and that in nitro-compounds attachment to the N atom occurs thus:

$$\begin{matrix} & R & \\ [:\underset{\cdot\cdot}{\ddot{O}}: & \ddot{N} & ::\ddot{O}:] \end{matrix}.$$

Nitrogen Trihalides

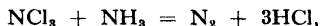
Nitrogen forms compounds with all the halogen elements, those with chlorine and iodine being the best known. They are endothermic compounds which are explosive, chloride of nitrogen being a very dangerous substance. These compounds are prepared by the action of the halogens, or of acids of the type HOX, on ammonia or ammonium salts.

Nitrogen trichloride is obtained as a heavy, oily liquid by passing chlorine into a concentrated solution of ammonium chloride, or by suspensing a lump of ammonium chloride in a concentrated solution of hypochlorous acid. The following reactions occur:

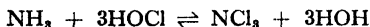
$$3Cl_2 + 3H_2O \rightleftharpoons 3HCl + 3HOCl.$$
$$NH_4Cl + 3HOCl \rightleftharpoons NCl_3 + 3H_2O + HCl.$$

If, however, chlorine reacts with ammonia gas or solution, nitrogen results, together with ammonium chloride thus:

$$3Cl_2 + 8NH_3 = N_2 + 6NH_4Cl;$$

for since NCl_3 reacts with moist NH_3 thus:

$$NCl_3 + NH_3 = N_2 + 3HCl,$$

it cannot be formed unless the gases are anhydrous.

The reversible reaction

$$NH_3 + 3HOCl \rightleftharpoons NCl_3 + 3HOH$$

is interesting, since the action of water on nitrogen chloride is a case of hydrolytic reduction, analogous to the acidic hydrolysis of nitrilosulphonic acid, $N(SO_3H)_3$, in which ammonia is generated. NCl_3 can hardly therefore be considered to be

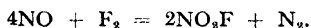
the chloride of orthonitrous acid, since no nitrous acid is produced in its hydrolysis.

The boiling points of some halogen compounds of nitrogen are here tabulated.

X.	NX_3	NHX_2	NH_2X	NOX	NO_2X
F	−119°	−65°	−77°	−59·9°	−72·4°
Cl	ca. 71°	?	?	−6°	−15°
Br	—	?	?	−2°	—
I	solid	—	—	—	—

Nitrogen trifluoride, NF_3, is formed by the exothermic reaction of fluorine and gaseous ammonia, or, accompanied by NH_2F and NHF_2, by the electrolysis of NH_4HF_2 (Ruff, 1928). It is a colourless, poisonous gas showing a remarkable contrast in properties to the other trihalides, being non-explosive and non-reactive with water or caustic soda. When sparked with hydrogen it reacts violently to give nitrogen and hydrogen fluoride. The other two colourless gases, NH_2F and NHF_2 are more reactive, the first reducing Fehling's solution and the second forming $NaNF_2$ with sodium.

Colourless, gaseous oxyfluorides, NO_2F and NOF, **nitroxyl-** and **nitrosyl-fluoride** respectively, have been prepared (Ruff, 1932), and are more stable than the corresponding chlorine compounds. Nitroxyl fluoride is prepared thus:

$$4NO + F_2 = 2NO_2F + N_2.$$

The parallel reaction with chlorine and bromine forms the *nitrosyl* derivatives. With water, NO_2F yields nitric, nitrous and hydrofluoric acids, while NOF reacts to give nitric and hydrofluoric acids, and nitric oxide.

Nitrogen iodide.—By the action of iodine on aqueous ammonia the compound $N_2H_3I_3$ is obtained as a coloured crystalline explosive substance, which is decomposed by water in the same way as chloride of nitrogen. Thus the reactions are:

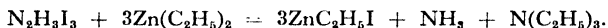
$$3I_2 + 3H_2O \rightleftharpoons 3HI + 3HOI \quad \text{and}$$
$$2NH_3 + 3HOI \rightleftharpoons N_2H_3I_3 + 3H_2O.$$

The final products of the action of water on $N_2H_3I_3$ are ammonium iodide and iodate, formed by the self-oxidation and reduction of ammonium hypoiodite, NH_4OI.

This compound is best prepared, however, by adding iodine chloride to ammonia solution at 0°.

$$ICl + 2NH_3 + H_2O = NH_4OI + NH_4Cl$$
$$3NH_4OI = N_2H_3I_3 + NH_3 + 3H_2O.$$

According to Silberrad * this substance has the constitution $NH_3 : NI_3$, since it reacts thus with zinc ethyl:

$$N_2H_3I_3 + 3Zn(C_2H_5)_2 = 3ZnC_2H_5I + NH_3 + N(C_2H_5)_3.$$

Nitrogen tri-iodide, NI_3, has been prepared (Cremer, 1930), by the action of dry ammonia on $KIBr_2$, the black explosive compound being washed free from soluble salts.

$$3KIBr_2 + 4NH_3 = 3KBr + 3NH_4Br + NI_3.$$

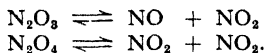
With gaseous ammonia it forms compounds NI_3, xNH_3, where $x = 1$ to 12, the mono-ammine being the most stable.

Halogen Azides.—**Iodine azide,** IN_3, is formed by the reaction of silver azide, AgN_3, and iodine. It is a white, powerfully explosive solid, which in aqueous solution hydrolyses to hydrazoic and hypoiodous acids.

Chlorazide, ClN_3, is a colourless, detonating gas.

Oxides of Nitrogen, N_2O, NO, N_2O_3, and N_2O_4

All these oxides can be obtained from nitric acid by the action upon it of metals or other reducing agents. The two latter can only exist in the state indicated by the above formulæ at low temperature. With rise of temperature dissociation takes place as follows:

$$N_2O_3 \rightleftharpoons NO + NO_2$$
$$N_2O_4 \rightleftharpoons NO_2 + NO_2.$$

N_2O and NO, **nitrous** and **nitric oxides** respectively, are neutral oxides; for although N_2O is formed from hyponitrous

* *Chem. Soc. Proc.*, **284**, 192.

acid by loss of water, it is incapable of combining with water or bases to form this acid or its salts. Nitric oxide is essentially an unsaturated substance, for although it does not form double molecules like NO_2, it combines with liquid nitrogen peroxide at low temperature to form N_2O_3, and with chlorine to form nitrosyl chloride.

Nitric oxide can be condensed to a colourless liquid which boils at $-153{\cdot}6^\circ$ under atmospheric pressure, whilst liquid nitrous oxide boils at -88°.

Nitrous and nitric oxides are both endothermic compounds, their heats of formation being -177 K and -216 K respectively. Like other endothermic compounds they can be detonated with mercury fulminate.

Dinitrogen trioxide, N_2O_3, exists as an indigo-blue liquid at low temperature. When this liquid evaporates it dissociates almost completely into NO and NO_2. It has been shown by Baker and Baker,* however, that perfectly dry nitrogen trioxide evaporates without dissociation, and that the gas contains some polymerized molecules, probably of N_4O_6. N_2O_3 is the anhydride of nitrous acid, and dissolves in water at 0° to form a blue liquid which contains the acid, but owes its colour to the anhydride.

Dinitrogen tetroxide or nitrogen dioxide exists as a white solid (N_2O_4) below -20°. The crystals melt at -12°, forming a yellow liquid, which becomes darker as the temperature rises. This liquid boils at 26°, giving a brown gas, which increases in intensity of colour with diminishing density on further heating, until finally it consists of molecules of NO_2 only. Nitrogen dioxide is a mixed anhydride, giving rise to nitrous and nitric acids on combination with water.

Nitrosyl chloride, NOCl, the chloride of nitrous acid, may be prepared by heating nitrosylsulphuric acid (chamber crystals) with sodium chloride:

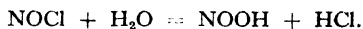
$$SO_2\left\langle{ONO \atop OH}\right. + NaCl = SO_2\left\langle{ONa \atop OH}\right. + NOCl.$$

* *Chem. Soc. Trans.* (1907), **91**, 1862.

It is also formed by the direct combination of nitric oxide and chlorine. It is present in aqua regia:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Nitrosyl chloride is a reddish-yellow gas at ordinary temperature, but it can be condensed to a red liquid, which boils at $-6°$. That it is the chloride of nitrous acid is shown by its manner of decomposition by water:

$$NOCl + H_2O = NOOH + HCl.$$

NX_5 Type

NH_5 is not known, nor is any pentahydride. The apex of the curve representing power of combination of elements with hydrogen is reached with methane, CH_4. The ammonium compounds might be considered as derivatives of the NH_5 type, but are better classified under the **first oxidized type, NH_4OH,** as salts derived from **ammonium hydroxide.**

Reference has been made, in the general introduction to this group, to the belief in the existence of NH_4OH, based upon the alkalinity of a solution of ammonia in water, which furnishes evidence of the presence of hydroxyl ions in solution. The analogy between the processes and products of neutralization of solutions of ammonia and potash or soda further supports this belief. Crystallohydrates, NH_3, H_2O and $2NH_3$, H_2O, exist at low temperature and these substances have been regarded as NH_4OH, and $(NH_4)_2O$, i.e. as ammonium hydroxide and oxide respectively.

It must not be supposed that all the ammonia which dissolves in water enters at once into chemical combination with it. An aqueous solution of ammonia approximately obeys Henry's law, which states that the amount of gas dissolved by a given quantity of a liquid varies directly as the pressure exerted by that gas on the surface of the liquid. Adherence to this law means that the molecules of gaseous NH_3 above the solution are in equilibrium with dissolved NH_3 *molecules*, these in turn being in equilibrium with the products of their reaction with water.

The solid, low-temperature hydrate, NH_3, H_2O, melting at $-79°$, may be represented as ammonium hydroxide, thus:

$$NH_3 + HOH \rightleftharpoons H_3N \rightarrow HOH,$$

but whether it exists in aqueous ammonia at ordinary temperature, and then by ionization and dissociation gives rise to alkalinity, or whether this result is caused by the direct reaction between ammonia and water without the formation of ammonium hydroxide, is difficult to decide. The low conductivity of the solution indicates paucity of ions.

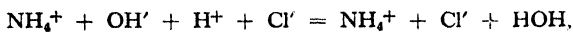
The simplest possible species and their dissociation equilibria in aqueous ammonia may be represented thus:

$$NH_3 + H_2O \rightleftharpoons [NH_4OH] \rightleftharpoons NH_4^+ + OH^-.$$

If the product enclosed in square brackets exists to any considerable extent, then ammonium hydroxide must be regarded as a weak base which is little ionized; but if this product is non-existent, or negligible, then it is possible to regard ammonium hydroxide as an intrinsically strong though unstable base. When the physical and chemical properties of the salts of the alkali metals are compared, the order is found to be: K, Rb, NH_4, Cs; and this lends countenance to the belief that NH_4^+ is a strong basic radicle, though some of these properties probably depend more on comparable ionic dimensions than on intrinsic chemical characteristics.

On the Lowry-Brönsted definition of a base as an acceptor, and an acid as a donor of hydrogen ions or protons, both NH_3 and OH^- are bases since both accept protons. The basic properties of ammonia, on this alternative view, might then depend on the extent to which it can deprive water of hydrogen ions, there being no need to assume the intermediate formation of non-ionized NH_4OH.

Similarly, when ammonia solution is neutralized with hydrochloric acid the reaction may be partly:

$$NH_4^+ + OH' + H^+ + Cl' = NH_4^+ + Cl' + HOH,$$

but will be chiefly: $NH_3 + H^+ + Cl' = NH_4^+ + Cl'$.

The work of Moore and Winmill (*J. Chem. Soc.*, 1907 and 1912), based on conductivities and partition coefficients using chloroform, enabled them to show the presence of three constituents in aqueous solutions of ammonia and amines. Thus, in aqueous ammonia at 18° C., the concentrations in mols ($\times 10^5$) per c.c. are:

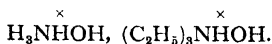
Total ammonia.	Free ammonia.	NH_4OH	NH_4^+
11·99	4·92	6·92	0·143

Hence weakly basic ammonium hydroxide exists, or something equivalent, for the experimental results cannot distinguish the exact compound here.

The alkyl-amines (mentioned previously as showing increased basicity) behaved similarly in aqueous solution. The undernoted dissociation constants ($\times 10^7$) measured at 18° C., indicate the basic power of the series of hydroxides where R is C_2H_5.

NH_4OH	RNH_3OH	R_2NH_2OH	R_3NHOH	R_4NOH
0·294	6·73	10·59	7·87	Ca. 10,000

The sudden increase in dissociating power developed in the last member, which is thus a base as strong as the alkali hydroxides, may be taken to mean that, so long as hydrogen can be co-ordinated, weakly basic hydroxides exist and may be represented, for example, thus:

$$H_3N\overset{\times}{H}OH,\ (C_2H_5)_3N\overset{\times}{H}OH.$$

This is an example of the hydrogen bond, in which hydrogen ($\times$) links two electronegative atoms. Theoretically, bivalent hydrogen, as in N—H—O, is not permissible, so that the linkage must be partly electrostatic, indicated by (···), with some increment of positive charge on the hydrogen atom. On these views, the protonic hydrogen is held between the electron pair of the nitrogen atom and the negative hydroxyl in a structure such as: $H_3N\cdots H\cdots OH$. Hence, the electrostatic character of the hydrogen bond will hinder the dissociation of ammonium hydroxide.

Reference has frequently been made in previous chapters to the hydrolysis of salts in solution. Thus it has been seen that normal salts of strong acids with weak bases react acid, and that similar salts of strong bases with weak acids react alkaline in aqueous solution; aluminium sulphate and sodium carbonate serve respectively as examples. Ammonium salts undergo hydrolysis when their solutions are boiled, in accordance with the law of mass action, and since ammonia gas escapes these solutions invariably become acid. It has been shown by Veley * that the acidity produced by hydrolysis and loss of ammonia at equivalent dilution varies from an inappreciable amount with the bromide and chloride, salts of strong acids, to a moderate degree with the sulphate and chlorate; and that the largest amount of decomposition takes place with the salts of weak organic acids, such as succinic and citric acids. Thus the retention of ammonia depends directly on the strength of the acid with which it is combined, the quantitative results of hydrolysis following the order of the affinity constants of the acids.

The type $NH_3(OH)_2$ is not represented, though derivatives of the anhydrous type NX_3O exist; they are the oxyamines, to which reference has already been made.

No representatives of the type $NH_2(OH)_3$ are known. It may be pointed out that this degree of oxidation corresponds in phosphorus with hypophosphorous acid, PH_2OOH, which may be considered a dehydration product of hypothetical $PH_2(OH)_3$.

The type $NH(OH)_4$ corresponds in its dehydrated form NHO_2 with the nitro-bodies. Such substances may be considered as derived from nitric acid by reduction, since the reaction,

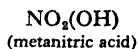
$$R \cdot H + HO \cdot NO_2 = R \cdot NO_2 + HOH,$$

shows the conversion of the replaced hydrogen of the body

* *Chem. Soc. Trans.* (1905), **87**, 26. See also E. G. Hill, *Chem. Soc. Trans.* (1906), **89**, 1273.

undergoing nitration into a constituent of the water molecule, a process of oxidation.

Of the three types representing **nitric acid,**

$N(OH)_5$	$NO(OH)_3$	$NO_2(OH)$
(orthonitric acid)	(mesonitric acid)	(metanitric acid)

only the last is certainly known. It is true that hydrates, such as HNO_3, $2H_2O$ and HNO_3, H_2O, exist, to which the first two formulæ might be attributed; but inasmuch as these compounds are unstable, it is doubtful whether the above formulæ can correctly be applied to them. The monohydrate may be H_3NO_4, since its X-ray pattern resembles that of H_3PO_4. Moreover, the salt Na_3NO_4 has been prepared and confirmed by X-ray analysis; it is unstable to water.

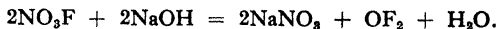
The chloride of nitric acid, NO_2Cl, **nitroxyl** or **nitryl chloride,** is said to be formed by the direct union of nitrogen dioxide and chlorine, but has been obtained pure by the reaction of nitrosyl chloride with ozone:

$$NOCl + O_3 = NO_2Cl + O_2.$$

It is a gas, condensing to a colourless liquid at $-15°$, and decomposing about 100° to give nitrogen dioxide and chlorine. Like all acid chlorides it is decomposed by water, thus:

$$NO_2Cl + H_2O = NO_2OH + HCl.$$

By passing fluorine into anhydrous nitric acid at room temperature, Cady (1934) obtained *nitrogen trioxyfluoride*, NO_3F, as a colourless irritant gas (B.P. $-45{\cdot}9°$, M.P. $-175°$). Both liquid and solid are explosive. It is non-reactive with dry glass. With water, it gives oxygen, fluorine monoxide, hydrofluoric and nitric acids, and reacts with caustic soda thus:

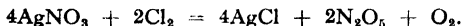
$$2NO_3F + 2NaOH = 2NaNO_3 + OF_2 + H_2O.$$

The structure assigned to it is $O_2N—O—F$.

The last dehydration product of orthonitric acid, **nitric**

anhydride, is obtained as a white, deliquescent crystalline substance by distilling anhydrous nitric acid with phosphoric oxide:

$$P_2O_5 + 2NO_2OH = 2HPO_3 + NO_2—O—NO_2.$$

It was originally prepared, however, by passing dry chlorine over dry silver nitrate, gently heated:

$$4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2.$$

Nitrogen trioxide, NO_3, is obtained as a white solid (Schwarz, 1935), when a glow discharge is passed through a low-pressure mixture of nitrogen dioxide and oxygen cooled by liquid air. The substance slowly decomposes into its generators above $-142°$. It reacts with water to give oxygen, nitrous and nitric acids, and is thus not a true acidic oxide. It liberates iodine slowly from potassium iodide in dilute HNO_3 solution. Its structure is tentatively, $O \leftarrow NO_2$.

The green solid formed by nitric oxide and liquid air, and formerly called nitrogen hexoxide, is empirically, N_3O_4. It is probably a peroxidized polymer of nitric oxide.

PHOSPHORUS

The molecules of nitrogen and phosphorus differ widely from one another. The molecules of nitrogen are diatomic; for, whilst the constituent atoms are firmly united together, so that the molecule resists disruption and is chemically inert, no tendency is shown towards further condensation; and the element becomes liquid only at very low temperature.

The molecules of phosphorus vapour are tetratomic for temperatures considerably above the boiling-point of the element; only when the vapour is heated very strongly does dissociation into diatomic molecules take place. Phosphorus, too, is easily condensed, its boiling-point and melting-point under atmospheric pressure being 287° and 44° respectively, whilst those of nitrogen are $-194°$ and $-214°$. Phosphorus, further, polymerizes, with production of allotropic forms.

Allotropy of phosphorus.—The two well-known forms of phosphorus are white or ordinary phosphorus, and red phosphorus, obtained by heating the white form to 250° out of contact with air. To these are to be added " metallic ", rhombohedral, or Hittorf's phosphorus, formed by crystallizing the element from its solution in molten lead, and Schenck's scarlet phosphorus, obtained when phosphorus is heated with its tribromide, and sometimes employed for making matches.

The question of the purity of these different forms arises. Red phosphorus having a density of 2·106 is not a single substance, for its physical properties and heat of combustion are not constant; it is probably a solid solution of white phosphorus in the metallic variety.* " Metallic " phosphorus may, however, be obtained without the use of lead by heating ordinary phosphorus in a sealed tube at 530°; and it is a definite allotropic form. Scarlet phosphorus may also be obtained pure by heating the tribromide with mercury in a sealed tube at 100–170°,and is therefore a separate form of the element.† Recent work has revealed the existence of three other forms of phosphorus.

β-white phosphorus is formed when α-white phosphorus, i.e. ordinary phosphorus, is submitted to a pressure of 11,000 kgm. per square centimetre at 60°, and crystallizes from carbon disulphide at low temperature in the hexagonal system. It changes reversibly into the α-form, the transition temperature ranging from —76·9° at 1 kgm. per square centimetre to 64·4° at 12,000 kgm. per square centimetre pressure.‡

Black phosphorus is obtained by heating ordinary phosphorus to 200° under 12,000 kgm. per square centimetre pressure. It is a good conductor of heat and electricity. Density, 2·69; melting-point, 587·5°.

Violet phosphorus is formed when ordinary phosphorus, in presence of a trace of sodium as a catalyst, is heated to 200°

* Cohen and Olie, *Chem. Weekblad* (1909), **6**, 821

† Wolf, *Ber.* (1915), **48**, 1272.

‡ P. W. Bridgman, *J. Amer. Chem. Soc.* (1914), **36**, 1344.

under a pressure rising to 130,000 kgm. per square centimetre. Density, 2·348; melting-point, 589·5°.

Thus not fewer than six allotropic forms of phosphorus are recognized.

ALLOTROPIC FORMS OF PHOSPHORUS

Form.	Density.	Melting-point.	Description.
α-white phosphorus	1·83	44·3°	Ordinary, waxy phosphorus, rhombic dodekahedra.
β-white phosphorus	—	—	Hexagonal crystals.
Scarlet phosphorus	2·0	—	—
Metallic phosphorus	2·316	—	Rhombohedral crystals.
Black phosphorus	2·69	587·5°	—
Violet phosphorus	2·348	589·5°	—

Although red phosphorus is not a definite allotropic form of the element, the conditions of its formation from and transformation into the white form are important. The transition from white to red phosphorus is an exothermic reaction, 27,300 calories being evolved per gramme-atom transformed. Conversely, this amount of heat would be absorbed in the conversion of red into white phosphorus. Ordinarily, however, the transformation is regarded as *monotropic*, i.e. proceeding in one direction only, rather than *enantiotropic*, or reversible. For, when red phosphorus is heated above 250° to transform it into the white variety, it is found to sublime about 290°, producing a vapour which, however, condenses into white phosphorus. Nevertheless, if red phosphorus is heated in a sealed tube so as to be under the high pressure of its own vapour, it is seen to form a nearly colourless liquid at 610°, from which on cooling red particles begin to separate at 580°, whilst the whole turns red at 570°. Thus the change from white to red phosphorus is seen to be enantiotropic under pressure, the transition temperature being about 600°.

Hydrides of Phosphorus

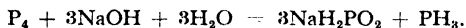
Five hydrides of phosphorus are known:

		M. P.		B. P.
PH_3	gaseous hydrogen phosphide..	$-133°$	....	$-85°$
P_2H_4	liquid ,, ,, ..	$-10°$	....	$57°$
$P_{12}H_6$	solid ,, ,, ..	—	....	—
* P_5H_2	,, ,, ,, ..	—	....	—
† P_9H_2	,, ,, ,, ..	—	....	—

PH_3 is the analogue of ammonia, and P_2H_4 that of hydrazine, but no nitrogen analogue of $P_{12}H_6$, P_5H_2, or P_9H_2 is known.

Phosphine, PH_3, like ammonia, can be obtained by the hydrolysis of its halide salts. Alkalis or water may be used; but whereas ammonium chloride yields very little ammonia when boiled with water, phosphonium iodide is easily and completely hydrolyzed by cold water. This difference is due to the slightly basic character of phosphine as compared with ammonia, and the accompanying slight stability of its salts, together with the small solubility of phosphine in water.

Phosphine is usually prepared, however, by boiling ordinary phosphorus with caustic alkali solution. The following is the reaction, to which nitrogen furnishes no analogy:

$$P_4 + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

This, however, does not represent all that happens, for some hydrogen is produced and a certain amount of P_2H_4 is formed which renders the PH_3 spontaneously inflammable.

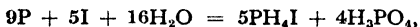
Phosphine is produced by the action of dilute acid on metallic phosphides (cf. H_2S), and also by heating hypophosphorous and phosphorous acids and their salts.

Phosphine is a powerful reducing agent, precipitating mixtures of metal and phosphide from solutions of cupric and silver salts. It is more readily decomposed by electric sparks than ammonia, and much more inflammable than this gas, its temperature of ignition being so low that it may sometimes

* Hackspill, *compt. rend.* (1913), **156**, 1466.
† Stock, Böttcher, and Lenger, *Ber.* (1909), **42**, 2847.

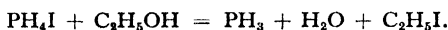
be ignited by the heat of friction caused by removal of the stopper from a bottle containing it. The final products of its combustion are phosphoric oxide and water.

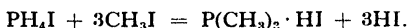
The fact that it is only slightly soluble in water, and that its solution is not alkaline, shows that the basic properties of phosphine are of the feeblest possible description; it will, however, unite directly with hydrogen halides to form salts, the best known of which is **phosphonium iodide.** This compound, prepared by the action of water on an intimate mixture of phosphorus and iodine:

$$9P + 5I + 16H_2O = 5PH_4I + 4H_3PO_4,$$

crystallizes in colourless quadratic prisms which may be sublimed. It fumes in moist air owing to hydrolytic decomposition. Ammonia displaces phosphine:

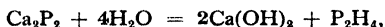
$$PH_4I + NH_3 = NH_4I + PH_3,$$

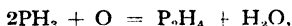
and alcohol decomposes the compound as follows:

$$PH_4I + C_2H_5OH = PH_3 + H_2O + C_2H_5I.$$

Phosphonium iodide is used as a reducing agent, and for the preparation of organic phosphines, for instance:

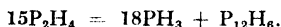
$$PH_4I + 3CH_3I = P(CH_3)_3 \cdot HI + 3HI.$$

Phosphonium bromide and chloride are even more unstable than the iodide. They are obtained by combination of phosphine with the hydrogen halides under pressure.

Liquid hydrogen phosphide, P_2H_4, may be obtained by the action of water on calcium phosphide, Ca_2P_2:

$$Ca_2P_2 + 4H_2O = 2Ca(OH)_2 + P_2H_4,$$

and results also from the oxidation of phosphine:

$$2PH_3 + O = P_2H_4 + H_2O,$$

which may be effected by means of nitric oxide. It is condensed by passage through a cooled tube to a colourless liquid

which boils at about 57°; this liquid is very unstable, and easily decomposes in sunlight into PH_3 and the solid hydride $P_{12}H_6$:

$$15P_2H_4 = 18PH_3 + P_{12}H_6.$$

The decomposition is promoted by hydrochloric acid, so that phosphine may be freed from the liquid hydride and deprived of its spontaneous inflammability by causing it to bubble through hydrochloric acid.

When the hydride $P_{12}H_6$ is heated *in vacuo* it evolves phosphine, leaving a second solid hydride, P_9H_2, thus:

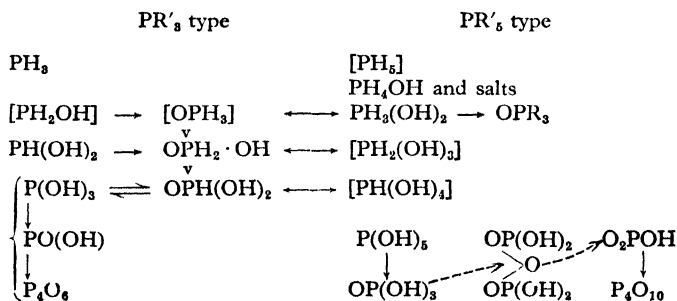
$$5P_{12}H_6 = 6P_9H_2 + 6PH_3.$$

Both of these solid hydrides are red. The hydride P_5H_2, obtained by decomposing the corresponding alkali phosphide with dilute acetic acid, is yellow.

The hydride P_2H_4 is not known to form any organic derivatives of the type $H_2P \cdot PHR$ analogous to phenylhydrazine, $H_2N \cdot NHC_6H_5$. Diphospho derivatives containing the grouping —P=P—, analogous to the diazo-grouping —N=N—, have been obtained; for instance, $C_6H_5P : PC_6H_5$, as well as $C_6H_5P : POH$; but these compounds do not resemble the corresponding nitrogen derivatives.

Oxygen Derivatives of Phosphorus

The oxygen derivatives of phosphorus are shown in the following scheme:

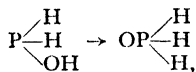
	PR′$_3$ type		PR′$_5$ type		
PH_3			$[PH_5]$		
			PH_4OH and salts		
$[PH_2OH]$ →	$[OPH_3]$	⟷	$PH_3(OH)_2$ →	OPR_3	
	v				
$PH(OH)_2$ →	$OPH_2 \cdot OH$	⟷	$[PH_2(OH)_3]$		
	v				
$P(OH)_3$ ⇌	$OPH(OH)_2$	⟷	$[PH(OH)_4]$		
↓					
$PO(OH)$			$P(OH)_5$	$OP(OH)_2$ ⇢	O_2POH
↓			↓	$>O$	↓
P_4O_6			$OP(OH)_3$ ⇢	$OP(OH)_2$	P_4O_{10}

In addition to the above, a suboxide, P_4O, is said to exist; there is also an oxide, $(PO_2)_n$, together with an acid, H_2PO_3, corresponding with the same degree of oxidation.

Phosphorus suboxide, or **tetritoxide**, P_4O, is said to be formed when finely divided white phosphorus is digested with one volume of 10-per-cent caustic-soda solution, and two volumes of alcohol. The solution becomes dark red, and when it is acidified with hydrochloric acid the supposed suboxide is obtained as a dark-yellow or reddish powder. The same product is obtained when yellow phosphorus is heated with liquid ammonia and the resulting amide is decomposed by water thus: $2P_2NH_2 + H_2O = P_4O + 2NH_3$. It has been shown, however, by Chapman, Lidbury, and Burgess * that the product of the first reaction contains more phosphorus than corresponds with the formula P_4O; and that it probably consists of impure red phosphorus containing oxygen, hydrogen, and other impurities. A. Stock also doubts the existence of P_4O.†

Corresponding with the unknown oxide PO and the liquid hydride P_2H_4 is the iodide $\mathbf{P_2I_4}$, obtained by bringing the elements together in theoretical proportions in carbon disulphide solution, and evaporating. This iodide is a yellow, crystalline mass, melting at 110°, and giving a vapour density corresponding with the above formula.

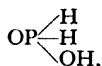
Phosphorus Derivatives of Type PR'_3

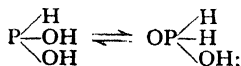
Considering the **type PR'_3**, the first oxidation product of PH_3 should be PH_2OH, corresponding with hydroxylamine, NH_2OH. This substance is not known, and it seems probable that it could not exist, or at least that it would be very unstable, for all hydroxylated derivatives of trivalent phosphorus show a tendency to undergo tautomeric change in such a manner as to become 4-covalent. Thus the change

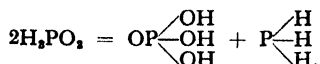
$$P\begin{cases}H\\H\\OH\end{cases} \rightarrow OP\begin{cases}H\\H\\H,\end{cases}$$

* *Chem. Soc. Trans.* (1899), **75**, 973, and (1901), **79**, 1235.
† *Chem. Zeit.* (1909), **33**, 1354.

were the compound known, would be consistent with the behaviour of known compounds, which are referred to below, the phosphorus atom becoming 4-covalent wherever possible in its oxygen compounds in accordance with its oxidizability. Indeed the type $OP\lessdot$ represents the most stable and characteristic grouping of the phosphorus atom. Numerous alkylated oxyphosphines, for instance $OP(CH_3)_3$, have been prepared by A. Michaelis.

The formula $PH(OH)_2$ corresponds with the stage of oxidation of hypophosphorous acid. Now this acid is strictly monobasic, and such a property does not accord well with the above formula, since the hydroxylic hydrogen will be replaced by metals in preference to the hydrogen attached directly to phosphorus. This makes it probable that the constitution of hypophosphorous acid is rather

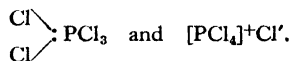
$$OP\begin{cases} H \\ H \\ OH, \end{cases}$$

or that possibly one of the hydrogen atoms is in a labile condition, thus:

$$P\begin{cases} H \\ OH \\ OH \end{cases} \rightleftharpoons OP\begin{cases} H \\ H \\ OH; \end{cases}$$

so that inorganic salts, at least of the dibasic form, cannot permanently exist. This tendency of phosphorus to pass over into the form $OP\lessdot$ is well brought out by the effect of heat on hypophosphorous acid and its salts, when phosphoric acid and phosphine are produced; thus:

$$2H_3PO_2 = OP\begin{cases} OH \\ OH \\ OH \end{cases} + P\begin{cases} H \\ H \\ H. \end{cases}$$

It will be observed that whilst hypophosphorous and hyponitrous acids may be conceived as derived from the same type

of oxidation, R''' $H(OH)_2$, similarity between their constitution ends here.

While nitrogen in its compounds exhibits a maximum co-valency of four, phosphorus, in PF_5 and, possibly, PCl_5, shows quinquivalency. The pentafluoride is stable to heat, but the pentachloride dissociates readily, whereas the oxychloride, $OPCl_3$, is stable. This appears to show that the phosphorus atom can retain in stable union four, but not five atoms in its periphery; this accords with the octet rule. On these considerations, PCl_5 has been formulated thus:

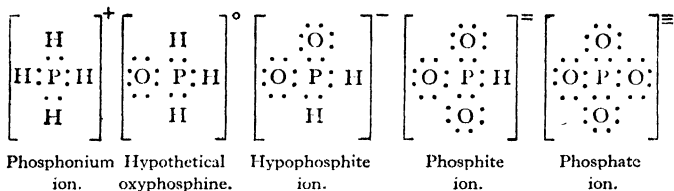
$$\begin{matrix} Cl \diagdown \\ \quad \vdots PCl_3 \\ Cl \diagup \end{matrix} \quad \text{and} \quad [PCl_4]^+Cl'.$$

In the first formula Prideaux identifies the reactivity of two chlorine atoms with the presence of mono-electronic links for which Sugden has obtained parachor evidence, the other three chlorine atoms being covalently linked. According to Sidgwick, however, the parachor change on which Sugden relies may be due to the uncertain influence of a ten electron group; in effect it may be evidence for normal 5-covalency in PCl_5. As regards the second formula, the zero dipole moment of PCl_5 points to an electrical symmetry not possible with this structure.

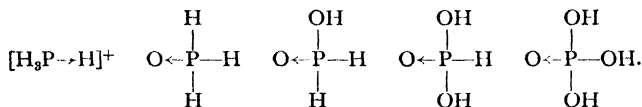
Quinquivalent phosphorus is definitely established by PF_5, but from its limited appearance it would seem to be unstable when achieved by a ten electron group.

On modern theory, the characteristic grouping, $OP\equiv$, indicates the superior stability, in oxy-compounds, of the electron octet, the oxygen not being linked to phosphorus by a double bond, as in the older theory, but rather co-ordinated thereto, thus: $O\leftarrow P\equiv$. Although phosphorus has now become 4-covalent, it is still true that, of its octet electrons, five are provided by the phosphorus atom itself. Hence, following Grimm and Sommerfeld, it may be regarded as exhibiting quinquivalency while making use of the stability conferred by an octet of electrons.

The electronic formulæ for phosphonium, oxyphosphine, and the ions of the phosphorus oxyacids are as follows:

```
[    H    ]+  [     H    ]°  [    ..     ]-  [    ..     ]=  [    ..     ]≡
[    ..   ]   [  ..  ..  ]   [   :O:     ]   [   :O:     ]   [   :O:     ]
[ H:P:H   ]   [ :O: P:H  ]   [ .. ..     ]   [ .. ..     ]   [ .. .. ..  ]
[    ..   ]   [  ..  ..  ]   [:O: P: H   ]   [:O: P: H   ]   [:O: P :O:  ]
[    H    ]   [     H    ]   [ .. ..     ]   [ .. ..     ]   [ .. .. ..  ]
                             [    H      ]   [   :O:     ]   [   :O:     ]
                                             [    ..     ]   [    ..     ]
```

Phosphonium ion. Hypothetical oxyphosphine. Hypophosphite ion. Phosphite ion. Phosphate ion.

or, using Sidgwick's symbol for co-ordination, their relationship is shown thus (the acids being undissociated):

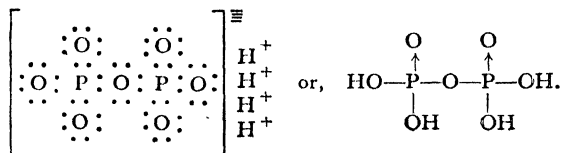
$$[H_3P \rightarrow H]^+ \quad \begin{array}{c} H \\ | \\ O\leftarrow P-H \\ | \\ H \end{array} \quad \begin{array}{c} OH \\ | \\ O\leftarrow P-H \\ | \\ H \end{array} \quad \begin{array}{c} OH \\ | \\ O\leftarrow P-H \\ | \\ OH \end{array} \quad \begin{array}{c} OH \\ | \\ O\leftarrow P-OH. \\ | \\ OH \end{array}$$

Since the phosphorus atom provides five electrons, the oxygen atom six, and each hydrogen atom one, the number of electrons provided is just enough in the case of OPH_3, which is thus represented as a neutral compound.

When an oxygen atom replaces a hydrogen atom, however, an electron must be supplied from outside, because the oxygen atom, having only six electrons in its shell, contributes none to the bond between itself and the phosphorus atom. Consequently, the hypophosphite ion, on account of its single imported electron, has a single negative charge upon it and is monobasic; whilst, from a similar cause, the phosphite and phosphate ions are respectively di- and tri-basic.

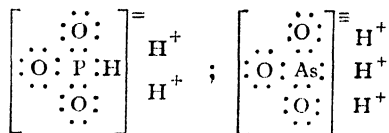
Pyrophosphoric acid is represented thus:

```
[     ..      ..        ]≡
[    :O:     :O:        ]   H+
[ ..  ..  ..  ..  ..    ]   H+
[:O: P :O: P :O:        ]   H+
[ ..  ..  ..  ..  ..    ]   H+
[    :O:     :O:        ]
[     ..      ..        ]
```

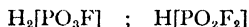
or,

$$\begin{array}{c} O \quad\quad O \\ \uparrow \quad\quad \uparrow \\ HO-P-O-P-OH. \\ | \quad\quad | \\ OH \quad\quad OH \end{array}$$

It is tetrabasic, the anion having a quadruple negative charge, because, of the 56 electrons present, only 52 (i.e. $7 \times 6 + 2 \times 5$) are provided by the phosphorus and oxygen atoms, the other four being derived from the ionizable hydrogen atoms.

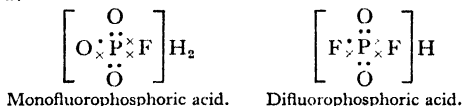
The difference in basicity between phosphorous and arsenious acids is represented thus:

$$\left[\begin{array}{ccc} & :\ddot{O}: & \\ :\ddot{O}: & \ddot{P} & :H \\ & :\ddot{O}: & \end{array}\right]^{=} \begin{array}{c} H^+ \\ H^+ \end{array} \quad ; \quad \left[\begin{array}{cc} & :\ddot{O}: \\ :\ddot{O}: & \ddot{As}: \\ & :\ddot{O}: \end{array}\right]^{\equiv} \begin{array}{c} H^+ \\ H^+ \\ H^+ \end{array}$$

Here the chemical difference is due to the strong tendency of the phosphorus atom, unlike that of arsenic, to co-ordinate four other atoms. This would also explain why arsenic does not form the analogue of PH_4Cl.

Of comparable structure are the mono- and di-fluorophosphoric acids

$$H_2[PO_3F] \quad ; \quad H[PO_2F_2]$$

obtained by Lange (1928, 1929) by heating H_3PO_4 and NH_4F, which gives the ammonium salts, or by dissolving P_2O_5 in strong aqueous HF, whereby the free mono-acid is produced.

$$\left[\begin{array}{c} O \\ O \times \ddot{P} \times F \\ O \end{array}\right] H_2 \qquad \left[\begin{array}{c} O \\ F \times \ddot{P} \times F \\ O \end{array}\right] H$$

Monofluorophosphoric acid. Difluorophosphoric acid.

The di-fluoro-acid is isolated as its " nitron " salt, and gives alkali and cadmium salts, e.g. $Cd(O_2PF_2)_2$ resembling perchlorates. Salts of the mono-fluorinated acid are analogous to sulphates, e.g. $Ag_2[PO_3F]$; $(NH_4)_2[PO_3F]$. Salts of both acids are stable in neutral solution, those of the mono-acid being stable to dilute alkali.

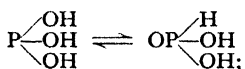
At the same time, hexafluorophosphoric acid $H[PF_6]$ or its salts may be obtained, though the latter are preferably obtained by the action of PCl_5 on alkali fluorides. Salts of this acid

are stable to boiling alkali, while salts of HBF_4 and H_2SiF_6 are thus readily decomposed. Similar hexa-compounds are given by arsenic and antimony.

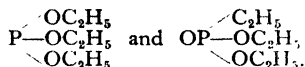
Hypophosphorous acid, H_3PO_2, may be obtained in a crystalline form by decomposing its barium salt with dilute sulphuric acid and evaporating the solution. It melts at 17°, and on being heated forms PH_3 and H_3PO_4. It is a powerful reducing agent, precipitating gold, silver, and mercury from their salts. It is distinguished from phosphorous acid, which behaves in a similar manner, by the solubility of its barium salt, and by precipitating cuprous hydride, Cu_2H_2, as a red powder, when warmed with acidified copper-sulphate solution.

Neither the anhydride nor the chloride of hypophosphorous acid is known.

The type $P(OH)_3$ represents symmetrical phosphorous acid. As regards the existence of a substance of this constitution, the following remarks may be made. Phosphorous acid is always dibasic in its solid inorganic salts, although Na_3PO_3 is supposed to exist in solution, and the ester $P(OC_2H_5)_3$ is known. The dibasicity of this acid may be explained by assuming that ionization proceeds only as far as 2H and HPO_3, since it is well known that polybasic acids are completely ionized with difficulty. Phosphoric acid, for instance, is ionized into H and H_2PO_4; but phosphoric acid is tribasic. Arsenious acid is even tribasic, since Ag_3AsO_3 is known, although it is probably a weaker acid than phosphorous acid. It would appear, therefore, that the reason for the dibasicity of this acid in its inorganic salts must be sought in another direction. All the facts are satisfactorily explained by supposing that phosphorous acid undergoes the following tautomeric change:

$$P\begin{cases}OH\\OH\\OH\end{cases} \rightleftharpoons OP\begin{cases}H\\OH\\OH;\end{cases}$$

so that its dibasicity depends on the tendency for self-oxidation manifested by phosphorus compounds. Correspond-

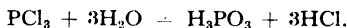
ing with these two formulæ are the isomeric ethyl esters:

$$P \begin{cases} OC_2H_5 \\ OC_2H_5 \\ OC_2H_5 \end{cases} \quad \text{and} \quad OP \begin{cases} C_2H_5 \\ OC_2H_5 \\ OC_2H_5. \end{cases}$$

Phosphorous acid when heated breaks up in a similar way to hypophosphorous acid, thus:

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

Phosphorous anhydride, P_4O_6, is produced, together with phosphoric anhydride, by the slow combustion of phosphorus in a tube through which air is drawn. It may be obtained in crystals which melt at 22·5°, and boils at 173° in an indifferent atmosphere. It forms phosphorous acid by combination with cold water, but hot water decomposes it, producing red phosphorus, phosphine, and phosphoric acid. When heated gently it burns, forming phosphoric oxide, but when quickly heated to 440°, it decomposes into red phosphorus and phosphorus tetroxide. Determination of vapour density leads to the formula P_4O_6.

Phosphorous acid, H_3PO_3, is formed by the combination of water with its anhydride, by the slow oxidation of phosphorus in moist air, or by the decomposition of the chloride of the acid by cold water:

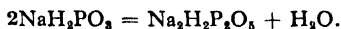
$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

After removal of water and hydrochloric acid by evaporation the phosphorous acid crystallizes as a deliquescent mass which melts at 71°. A solution of the acid or its salts reduces salts of gold, silver, and mercury, and precipitates sulphur from sulphurous acid.

Pyrophosphorous acid, $H_2(H_2P_2O_5)$, is formed from PCl_3 and H_3PO_3 by the reaction:

$$10H_3PO_3 + 2PCl_3 = 6H_4P_2O_5 + 6HCl.$$

It forms colourless needles melting at 38°. The sodium salt

is obtained by heating primary sodium phosphite to 160° thus:

$$2NaH_2PO_3 = Na_2H_2P_2O_5 + H_2O.$$

Metaphosphorous acid, HPO_2, is formed in crystals melting at about 10° when equal volumes of phosphine and oxygen interact under a pressure of 25 mm.:

$$PH_3 + O_2 = HPO_2 + H_2.$$

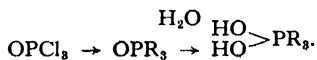
The **chloride of phosphorous acid, phosphorus trichloride,** PCl_3, is formed when phosphorus burns in chlorine, or when a current of dry chlorine is led over phosphorus. It is a colourless liquid, boiling at 76°. Cold water decomposes it, forming hydrochloric and phosphorous acids. Hot water gives phosphoric acid and lower oxides of phosphorus. It is susceptible of easy oxidation to phosphoryl chloride, $POCl_3$.

Phosphorus Derivatives of Type PR'_5

Phosphoric anhydride, or phosphoric oxide, P_4O_{10}, the product of the complete combustion of phosphorus in air or oxygen, is a white, amorphous, hygroscopic solid, which when heated yields a crystalline sublimate. It is a powerful dehydrating agent, combining with water to form meta- and orthophosphoric acids.

Concerning the hydroxylated products of quinquivalent phosphorus, it may be pointed out that of the hypothetical types, $PH_3(OH)_2$, $PH_2(OH)_3$, $PH(OH)_4$, the first represents a hydroxylated form corresponding with the oxyamines previously considered, and that the latter two correspond respectively with hydroxylated forms of hypophosphorous and unsymmetrical phosphorous acids.

With regard to the orthophosphoric type, $P(OH)_5$, although no salts of a pentabasic phosphoric acid are known, esters have been obtained and Michaelis has obtained corresponding organic hydroxylated derivatives of phosphoryl chloride:

$$OPCl_3 \rightarrow OPR_3 \xrightarrow{H_2O} {HO \atop HO}{>}PR_3.$$

Whilst $P(OH)_5$ and its salts do not appear to exist, the first dehydration product, $PO(OH)_3$, is stable at ordinary temperature, both in the solid state and in solution. It is therefore known as orthophosphoric acid.

Relations between the forms of phosphoric acid.— It was pointed out on page 116 that polybasic acids such as boric, phosphoric, and silicic acids form condensed or anhydro-acids by loss of water molecules between two or more molecules of the more completely hydrated acid. Phosphoric acid furnishes a well-known example of this phenomenon.

The existence of three forms of phosphoric acid, the ortho-, meta-, and pyroacid, was shown by Graham,* and it was believed by Sabatier, and by Fleitmann and Hennenberg † and others that polymerized forms of metaphosphoric acid exist of the type $(HPO_3)_n$ where $n = 2, 3, 4, 5, 6, 8$, and 10. The evidence for the existence of these forms depended, however, on methods of preparation, and composition and properties of salts, rather than on molecular weight determinations. The constitutional relationship between some possible forms of phosphoric acid is shown in what follows.

Dehydration of phosphoric acid may involve either a single molecule, thus:

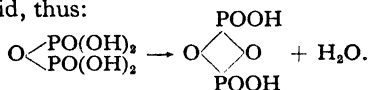
$$PO(OH)_3 = PO_2OH + H_2O,$$

or two molecules, thus:

$$\begin{matrix} PO(OH)_3 \\ PO(OH)_3 \end{matrix} = O\begin{matrix} \diagup PO(OH)_2 \\ \diagdown PO(OH)_2 \end{matrix} + H_2O,$$

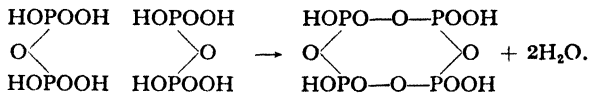
the product in the first case being metaphosphoric, and in the second, pyrophosphoric acid.

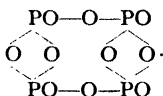
If a molecule of pyrophosphoric acid lost a molecule of water in the same sense as the original ortho-acid lost a molecule to form the pyro-acid, there would result dimetapnosphoric acid, thus:

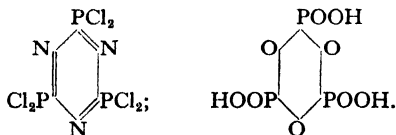
$$O\begin{matrix} \diagup PO(OH)_2 \\ \diagdown PO(OH)_2 \end{matrix} \rightarrow O\begin{matrix} \diagup POOH \diagdown \\ \diagdown POOH \diagup \end{matrix}O + H_2O.$$

* *Phil. Trans.* (1833), **52**, 253.

† *Compt. rend.* (1888), **106**, 63; (1889), **108**, 738, 804.

If two molecules were involved in this condensation instead of only one, there would result tetrametaphosphoric acid, thus:

```
HOPOOH   HOPOOH        HOPO—O—POOH
O<            >O   →   O<          >O  + 2H2O.
HOPOOH   HOPOOH        HOPO—O—POOH
```

It is now only a step, from the point of view of constitution, from tetrametaphosphoric acid to phosphoric anhydride, P_4O_{10}, which may be represented thus:

```
  PO—O—PO
 /  \  /  \
O   O  O   O·
 \  /  \  /
  PO—O—PO
```

The above illustrations do not, however, exhaust the possibilities of polymerization exhibited by this class of compounds. Instances of polymerization into threefold union are known among carbon compounds; for example, the conversion of aldehyde into paraldehyde and acetylene into benzene. Some phosphoric compounds display a like tendency. The compound $NPCl_2$, for instance, when formed from PCl_5 and NH_3 at a temperature of 175–200°, consists of molecules $(NPCl_2)_3$ which may be compared with trimetaphosphoric acid $(HPO_3)_3$. The constitution of these two compounds may be represented thus:

```
      PCl2                   POOH
    N//  \\N               O/    \O
    ||    |                 |     |
  Cl2P   //PCl2;       HOOP\     /POOH.
      \\ /                   \  /
       N                      O
```

Orthophosphoric acid, H_3PO_4, obtained as a crystalline mass by evaporating its solution, melts at 38°. Its aqueous solution is but slightly ionized, and freezing-point determinations show H_3PO_4 molecules to be present.* The

* Holt and Myers, *Chem. Soc. Trans.* (1911), 99, 389.

tribasicity of this acid is proved by the three sodium salts:

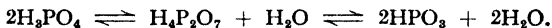
Primary sodium phosphate,			NaH_2PO_4, H_2O.
Secondary	,,	,,	Na_2HPO_4, $12H_2O$.
Tertiary	,,	,,	Na_3PO_4, $12H_2O$.

Corresponding calcium salts are:

$$CaH_4(PO_4)_2;\ CaHPO_4,\ 2H_2O;\ Ca_3(PO_4)_2.$$

Microcosmic salt is $NaNH_4HPO_4$, $4H_2O$; another important salt is $MgNH_4PO_4$, $6H_2O$; ferric phosphate, insoluble in acetic acid, is produced in the elimination of the phosphate radicle in analysis. Insoluble phosphates, such as those of calcium and ferric iron, are slowly hydrolyzed by water into an insoluble, more basic, constituent, and a soluble constituent which shows the presence of free acid. Soluble phosphates, e.g. those of sodium, also show marked hydrolysis in solution, so that whilst NaH_2PO_4 has an acid reaction, Na_2HPO_4 is slightly, and Na_3PO_4 strongly, alkaline. Solutions of the two former salts are employed as standard solutions of low acidity and alkalinity respectively, and when mixed in various proportions yield standards slightly removed on either side from the neutral point.

Pyrophosphoric acid, $H_4P_2O_7$, is obtained as an intermediate product either by the dehydration of the ortho-acid or the hydration of the meta-acid:

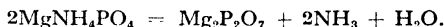
$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O \rightleftharpoons 2HPO_3 + 2H_2O.$$

The pyro-acid, obtained as a syrup by dehydrating the ortho-acid, consists in normal solution of complex molecules $(H_4P_2O_7)_4$ or $(H_4P_2O_7)_5$, but when prepared by decomposing lead pyrophosphate with hydrogen sulphide, the acid in aqueous solution consists of simple molecules $H_4P_2O_7$.* The syrupy solution of the pyro-acid yields mixed crystals of the ortho- and pyro-acid, so that the latter cannot be regarded as a stable

* Holt and Myers, *Chem. Soc. Trans.* (1911), 99, 390.

substance. Sodium pyrophosphate is obtained by igniting secondary sodium phosphate thus:

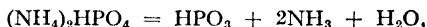
$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O;$$

magnesium ammonium phosphate similarly yields pyrophosphate:

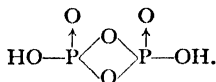
$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

Ortho- and pyrophosphate are distinguished by their silver salts: Ag_3PO_4 is yellow, $Ag_4P_2O_7$ white.

Normal and dihydrogen pyrophosphates exist, e.g. $Na_4P_2O_7$, $10H_2O$ and $Na_2H_2P_2O_7$, $6H_2O$. Pyrophosphates revert in solution to orthophosphates, slowly when cold, more quickly when heated.

Metaphosphoric acid, HPO_3, may be obtained by the action of moisture on phosphoric oxide, by heating glacial phosphoric acid to redness, by igniting one of the ammonium phosphates, thus:

$$(NH_4)_2HPO_4 = HPO_3 + 2NH_3 + H_2O,$$

or in solution by decomposing with hydrogen sulphide, lead metaphosphate suspended in water.

Obtained in aqueous solution by the last-named method it consists of simple molecules HPO_3; formed by ignition of glacial phosphoric acid to redness for a short time it consists of molecules $(HPO_3)_3$, which by prolonged ignition pass into $(HPO_3)_2$ molecules. Moreover, when obtained as vapour,* metaphosphoric acid is $(HPO_3)_2$ or

```
   O       O
   ↑  ⁄O\  ↑
HO—P<     >P—OH.
      \O⁄
```

Sodium metaphosphate glass, formed, for example, by ignition of primary sodium phosphate or microcosmic salt, is $(NaPO_3)_3$. Di- and trimetaphosphates appear to be the only polymerized forms of this acid for which molecular weight determinations

* Tilden and Barnett, *Chem. Soc. Trans.* (1896), 69, 158.

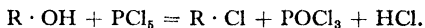
furnish evidence*, so that the more complex forms of the acid previously believed to exist may be disregarded. A metaphosphate in solution is distinguished from ortho- and pyrophosphate by coagulating egg-albumen in presence of acetic acid. Like pyrophosphates, metaphosphates gradually revert to orthophosphates in solution.

Chlorides of Phosphoric Acid

Phosphorus pentachloride, or **phosphoric chloride,** PCl_5, corresponds with the hypothetical ortho-acid, $P(OH)_5$, and phosphoryl chloride, or phosphorus oxychloride, $POCl_3$, with ordinary phosphoric acid; whilst $P_2O_3Cl_4$ is the chloride of pyrophosphoric acid, and PO_2Cl the chloride of metaphosphoric acid. Phosphorus pentachloride is prepared by the action of chlorine on the trichloride. It is a pale-yellow crystalline solid which fumes in moist air.

Whilst neither phosphoric oxide nor its hydration products lose oxygen when heated, phosphoric chloride dissociates into phosphorous chloride and chlorine at a moderate temperature. The superior stability of the oxide molecule is probably due to spatial relationships and to the greater power of persistence of the type $OP\lessgtr$, as compared with $Cl_2P\lessgtr$. It may be observed that phosphoryl chloride, $OP\begin{smallmatrix}\diagup Cl\\ - Cl\\ \diagdown Cl\end{smallmatrix}$, is not dissociated by heat, and also that the chlorine type of compound is more comparable with the hydrogen than the oxygen type, and that no pentahydride of phosphorus is known.

Phosphorus pentachloride is employed, especially in organic chemistry, for the substitution of Cl for OH, according to the following general reaction:

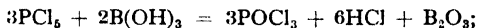
$$R \cdot OH + PCl_5 = R \cdot Cl + POCl_3 + HCl.$$

Phosphoryl chloride, or phosphorus oxychloride,

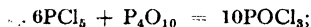
* Holt and Myers, *Chem. Soc. Trans.* (1911), **99**, 384; (1913), **103**, 532.

$POCl_3$, is the first product of the action of water on PCl_5:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

It may consequently be prepared by the use of boric acid, thus:

$$3PCl_5 + 2B(OH)_3 = 3POCl_3 + 6HCl + B_2O_3;$$

also by the combination of phosphoric oxide and chloride:

$$6PCl_5 + P_4O_{10} = 10POCl_3;$$

and by the direct oxidation of PCl_3. It is a colourless, mobile liquid, boiling at 107°, which is decomposed by water into phosphoric and hydrochloric acids.

Pyrophosphoryl chloride, $P_2O_3Cl_4$, is a colourless, fuming liquid, boiling at 210–215°; and thereby suffering partial decomposition into $POCl_3$ and P_4O_{10}. It is obtained, together with other products, by the oxidation at low temperature of phosphorus trichloride by nitrogen tetroxide.

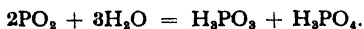
Metaphosphoryl chloride, PO_2Cl, is said to be formed as syrupy liquid when pyrophosphoryl chloride is distilled under reduced pressure:

$$P_2O_3Cl_4 = PO_2Cl + POCl_3.$$

It decomposes thus when heated: $3PO_2Cl = POCl_3 + P_2O_5$.

Phosphorosophosphoric oxide, $(PO_2)_n$, and **hypophosphoric acid,** H_2PO_3, remain to be considered.

Phosphorosophosphoric oxide is obtained by the partial combustion of phosphorus, and also from phosphorous oxide, which, when heated to 440°, decomposes into red phosphorus and $(PO_2)_n$. This latter compound forms colourless crystals which sublime *in vacuo* at 180°; its vapour density at about 1400° is 230, which corresponds nearly to the molecular formula P_8O_{16}. Its solution in cold or boiling water reduces mercuric and silver salts, and contains phosphorous and phosphoric acids:

$$2PO_2 + 3H_2O = H_3PO_3 + H_3PO_4.$$

Phosphorosophosphoric oxide is therefore a mixed anhydride,

and is in this respect analogous to nitrogen tetroxide, which dissolves in water to form nitrous and nitric acids.

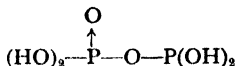
Hypophosphoric acid, which has the empirical formula H_2PO_3, is obtained by the slow oxidation of phosphorus in moist air, and may be separated from the other acids produced at the same time by forming the sparingly soluble sodium salt, $NaHPO_3$, $3H_2O$. The acid itself may be obtained in crystals containing one molecule of water, H_2PO_3, H_2O, and melting at 62°, by decomposing the barium salt with dilute sulphuric acid, and evaporating the filtered solution under reduced pressure. The molecular formula of hypophosphoric acid has been a matter of controversy. It was originally thought to be $H_4P_2O_6$, the sodium salt by means of which it is isolated being $Na_2H_2P_2O_6$, $6H_2O$.

Parravano and Marini * conclude from variations of the electric conductivity at varying dilutions that the two sodium salts are correctly represented by the formulæ $Na_2H_2P_2O_6$ and $Na_4P_2O_6$, rather than by $NaHPO_3$ and Na_2PO_3.

The salt $Na_3HP_2O_6$, $9H_2O$ might suggest the tetrabasicity of hypophosphoric acid, and the corresponding formula $H_4P_2O_6$, but this salt may be Na_2PO_3, $NaHPO_3$, $9H_2O$, with which may be compared the sesquicarbonate Na_2CO_3, $NaHCO_3$, $2H_2O$.

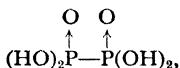
On the other hand, Rosenheim and co-workers (1906, 1908), from similar conductivity experiments, and from the molecular weights of alkyl esters determined ebulliscopically, concluded that the acid is H_2PO_3. A redetermination of the molecular weight of the ethyl ester by Arbusov (1931) gives the formula $Et_4P_2O_6$, which is confirmed (Bell and Sugden, 1933) by the fact that in salts of the acid, phosphorus is diamagnetic, whereas, in H_2PO_3, phosphorus would have an odd number of electrons, involving paramagnetism. Most probably the acid is $H_4P_2O_6$.

The constitution

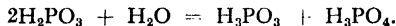
$$(HO)_2\text{—}\overset{\overset{\displaystyle O}{\uparrow}}{P}\text{—}O\text{—}P(OH)_2$$

* *Atti R. Accad. Lincei* (v), **15**, ii, 203.

has been attributed to hypophosphoric acid, in which this compound appears to be a mixed anhydride of phosphorous and phosphoric acids. If the acid possessed this constitution, its reducing properties would probably resemble those of phosphorous acid. It is distinguished, however, from the latter acid by the readiness with which it reduces acidified permanganate solution, and by this means it may be estimated.

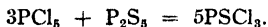
If, therefore, the molecular formula of hypophosphoric acid is $H_4P_2O_6$, its constitution is best represented by the formula

$$(HO)_2\overset{\overset{O}{\uparrow}}{P}-\overset{\overset{O}{\uparrow}}{P}(OH)_2,$$

which shows analogy with oxalic and dithionic acids; if, however, H_2PO_3 is the molecular formula, the constitution $OP(OH)_2$ represents an anomalous compound.

When heated with mineral acid, hypophosphoric acid is converted into phosphorous and phosphoric acids, thus:

$$2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4.$$

The Sulphides of Phosphorus

Several compounds of phosphorus and sulphur have been prepared by heating the elements together. The most important of these is the **pentasulphide,** P_2S_5, consisting of yellow crystals, which melt at 274–276° and distil unchanged. It is the thioanhydride of thiophosphoric acid, and unites with alkalis to form mono-, di-, and tri-thiophosphates, M_3PO_3S, $M_3PO_2S_2$, M_3POS_3, respectively; the complete thiophosphates, M_3PS_4, appear, however, to be unknown. The chloride, **thiophosphoryl chloride,** $SPCl_3$, is prepared by the interaction of PCl_5 and P_2S_5, thus:

$$3PCl_5 + P_2S_5 = 5PSCl_3.$$

The product is a colourless liquid, boiling at 125°.

Phosphorus sesquisulphide, P_4S_3, yellow rhombic prisms, melting at 166°, and soluble in carbon disulphide, is used in place of white phosphorus for making matches.

ARSENIC, ANTIMONY, AND BISMUTH

These three elements present a transition from non-metallic to metallic characters, since in arsenic non-metallic properties predominate, and in bismuth, metallic properties. Arsenic is closely allied to phosphorus in the properties of the element, and the types of compounds which it forms, and antimony similarly approximates to arsenic. Bismuth, however, shows a marked difference from the other two elements in the much more pronounced basic character of its oxides, and in the instability of its hydride, which, however, appears to be formed when acid acts on a bismuth-magnesium alloy, since bismuth is deposited when the evolved gas is passed through a tube heated locally.

Some physical constants are here given:

	Density.	M.P	B.P.
Arsenic ..	As_α 3·88, As_β 4·71, As_γ 5·73	500° under increased pressure	—
Antimony ..	Sb_α —, Sb_β 5·3, Sb_γ about 6·7	630°	Bright red heat
Bismuth ..	9·75	271°	About 1400°

The melting-point of arsenic under increased pressure is lower than that of antimony, and the former element is considerably more volatile than the latter, since it begins to sublime below 100°. Arsenic exists in three allotropic modifications, which may be designated, in the reverse order of their stability, as As_α, As_β, As_γ. This allotropy is distinctly a non-metallic characteristic, and indeed in the nature of its allotropic forms arsenic closely recalls phosphorus.

As_α is produced by subliming ordinary arsenic in a stream of CO_2 and quickly cooling the vapour; it is a sulphur-yellow powder, which is soluble in carbon disulphide, and is probably crystalline. It recalls ordinary or white phosphorus. When it is heated it passes quickly into As_β, or mirror arsenic,

which is generally described as amorphous, but is probably crystalline. Finally, both of these varieties pass, on strong heating, into ordinary crystalline or " metallic " arsenic, As_γ, which is analogous to " metallic " phosphorus.

Antimony and bismuth present a more unmistakably metallic appearance in the free state than arsenic, but antimony resembles arsenic in its allotropic forms. Sb_α is yellow like As_α, and is formed by oxidizing stibine below $-90°$; Sb_β, similarly produced at $-40°$, is an amorphous black powder, which passes on heating into the stable, greyish-white metallic form. " Explosive antimony ", deposited on an antimony cathode during the electrolysis of a concentrated solution of the trichloride in hydrochloric acid, is probably a solid solution of the trichloride in black antimony. Bismuth exists in two enantiotropic modifications, the transition temperature between them being 75° at 760 mm. pressure.

As regards the molecular condition of their vapours, these elements show a gradation of properties. Arsenic vapour, like phosphorus, is tetratomic at moderately low temperatures, but above 1600° dissociates into diatomic molecules. The density of antimony vapour at about 1600° shows that it is a mixture of diatomic and monatomic molecules. The vapour density of bismuth between 1600° and 1700° reveals a similar molecular state. Simple molecular constitution in the state of vapour is a criterion of the metallic state; the vapours of metals being, as far as is known, for the most part monatomic. This might be assigned to the high temperature required to vaporize them, but cryoscopic measurements also show monatomicity.

The behaviour of these elements towards acids is important. Hydrochloric acid has little or no action on arsenic, antimony, or bismuth in absence of air; in presence of air the chlorides are formed. Nitric acid oxidizes arsenic to arsenic acid, H_3AsO_4, and antimony to hydrated antimonious or antimonic oxide according to the strength of the acid; this metal therefore behaves like tin towards nitric acid. Dilute nitric acid dissolves finely-divided antimony, however; probably an ill-

defined nitrate is thus formed. When nitric acid acts upon bismuth the nitrate is formed in solution. Three degrees of metallic nature are here illustrated by the action of nitric acid

(i) formation of soluble oxyacid,
(ii) „ insoluble hydrated oxide,
(iii) „ soluble nitrate.

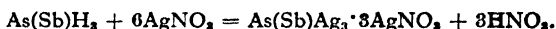
All three elements dissolve in hot concentrated, though not in dilute, sulphuric acid, with evolution of sulphur dioxide, and formation of sulphate, probably, in each case. Antimonious and bismuthous sulphates are well known. Arsenious sulphate, $As_2(SO_4)_3$, probably exists.

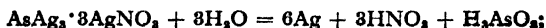
Hydrides of Arsenic and Antimony

The hydrides of this group have been discussed on p. 275; the properties of the simple hydrides of arsenic and antimony are further illustrated by the following facts:

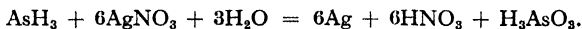
Arsine boils at $-58{\cdot}5°$ and solidifies at $-111°$.
Stibine „ $-17°$ „ „ „ $-88°$.

These hydrides are obtained by the action of hydrochloric acid on metallic arsenides and antimonides respectively, and are produced in a highly diluted state by the action of nascent hydrogen upon compounds of arsenic and antimony in solution, as in the familiar Marsh's test. The dissociation of the hydrides in this test is shown by the deposition of the solid elements in the heated tube. Stibine is more readily dissociated than arsine; and antimony, being less volatile, is deposited nearer the flame than arsenic. The hydrides are further distinguished by their behaviour towards silver nitrate. With solid silver nitrate arsine and stibine produce similar yellow compounds of silver arsenide or antimonide and nitrate (Gutzeit's test), thus:

$$As(Sb)H_3 + 6AgNO_3 = As(Sb)Ag_3{\cdot}3AgNO_3 + 3HNO_3.$$

The arsenic compound is decomposed by water, thus:

$$AsAg_3{\cdot}3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3AsO_3;$$

but the antimony compound yields $SbAg_3$ and $AgNO_3$ without reduction of the silver salt.

If arsine is passed through a dilute solution of silver nitrate, metallic silver is at once precipitated (Hofmann's test), whilst the arsenic goes into solution as arsenious acid, thus:

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + 6HNO_3 + H_3AsO_3.$$

In the case of stibine, however, silver antimonide is precipitated, together with some metallic silver resulting from the action of hydrogen on silver nitrate. This test serves to distinguish and separate arsenic from antimony.

The difference in behaviour in the two cases evidently depends on the superior oxidizability of arsine, which passes into solution as arsenious acid. In this respect the hydride of arsenic approximates to that of phosphorus, which is a very powerful reducing agent. That arsenic itself is more easily oxidized than antimony is shown by the solubility in hypochlorite solution of the deposit obtained in Marsh's test, the corresponding antimony deposit being insoluble.

No other hydride of antimony but SbH_3 is known; arsenic, however, forms the compound $\mathbf{As_2H_2}$, which is a silky solid, produced by the action of water on sodium arsenide, $AsNa_3$. Its phosphorus analogue, P_2H_2, is not known, and the existence of N_2H_2 is doubtful.

The type of hydrazine, N_2H_4, and liquid hydrogen phosphide, P_2H_4, is represented by **cacodyl**, $As_2(CH_3)_4$.

Oxygen Compounds of As, Sb, and Bi

The oxides of the types X_2O_3 and X_2O_5 are representative of the two main classes of compounds which these elements form. Some lower and intermediate oxides are, however, known.

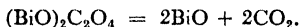
A suboxide of arsenic, As_2O, probably exists, and is said to be produced, together with the various allotropic forms of the element, when arsenic is sublimed in an open tube.

Corresponding with the unknown oxide, AsO, is the iodide, AsI_2, formed when AsI_3 is heated with arsenic in a sealed

tube in presence of carbon disulphide. This compound recalls the iodide of phosphorus, P_2I_4.

The existence of a suboxide of antimony is very doubtful.

Bismuth forms a **suboxide,** BiO or Bi_2O_2, which is obtained as a black precipitate by the reduction of a bismuth salt by an alkaline stannous solution. The same compound is formed by igniting basic bismuth oxalate out of contact with air:

$$(BiO)_2C_2O_4 = 2BiO + 2CO_2.$$

Bismuth dihalides, BiX_2, are also known.

A sulphur analogue of the R_2O_2 type exists in the case of arsenic. It is the disulphide, As_2S_2, which occurs naturally as **realgar.** Antimony and bismuth both form oxides, X_2O_4.

OXIDES OF THE TYPE X_2O_3 AND THEIR DERIVATIVES

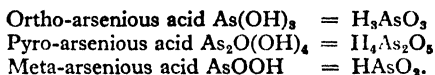
Arsenious oxide, As_4O_6, is analogous to phosphorous oxide on account of its molecular constitution, and the fact that it is an acidic anhydride. It also resembles phosphorous oxide in existing in more than one form. The vitreous form, which is transparent, is produced when ordinary "white arsenic" is heated to its temperature of sublimation. It passes into the octahedral form when kept at ordinary temperature. It is more soluble in water than the crystalline form, but a saturated solution gradually deposits octahedral crystals. Arsenious oxide also occurs in monoclinic crystals which separate from alkaline solution, and are isomorphous with a natural form of antimonious oxide.

The resemblance between phosphorous and arsenious oxides is slight; for whilst phosphorous oxide is unstable towards heat, arsenious oxide is quite stable, and sublimes unchanged; and whilst phosphorous oxide is easily soluble in water, arsenious oxide is very slightly soluble. The power of combining with water possessed by arsenious oxide is so slight that the acid itself has never been obtained, evaporation of its solution causing the separation of the oxide.

Arsenious oxide dissolves in sodium hydroxide and car-

bonate solutions, forming arsenites, though from hot concentrated solutions some of the oxide again separates on cooling; it also dissolves in hydrochloric acid, owing to the formation of arsenious chloride, though from a concentrated solution arsenious oxide gradually separates in well-formed crystals. The presence of the volatile arsenious chloride in such a solution is proved by its appearance in the liquid obtained by distillation.

Arsenious acid.—Arsenious oxide is slightly soluble in water, forming a solution with a feebly acid reaction. This solution contains ortho- or meta-arsenious acid. Salts corresponding with the unknown ortho-, pyro, and meta-arsenious acids, with the following formulæ, are known:

Ortho-arsenious acid $As(OH)_3 = H_3AsO_3$
Pyro-arsenious acid $As_2O(OH)_4 = H_4As_2O_5$
Meta-arsenious acid $AsOOH = HAsO_2$.

Salts of pyro- and meta-, as well as of ortho-arsenious acid, are obtained by precipitation or crystallization from solution, not by ignition. The alkali arsenites, which are soluble in water, are metasalts or salts in which H_3AsO_3 functions as a monobasic acid, as in NaH_2AsO_3; most pyro- and ortho-arsenites are insoluble. All arsenites are easily decomposed, since arsenious acid is very weak; carbonic acid or hydrogen sulphide suffices for this purpose. The soluble arsenites react alkaline, owing to hydrolysis. There is no reason to regard arsenic as other than trivalent in arsenious compounds, arsenic thus differing from phosphorus in analogous compounds.

Arsenious acid is a reducing agent, precipitating cuprous oxide from an alkaline cupric solution. It does not, however, possess such powerful reducing properties as phosphorous acid. Its reaction with iodine is well known. Arsenic in the condition of arsenious compounds may be reduced to the state of the element when in solution, as well as when heated in the solid state with reducing agents. For instance, a solution of stannous chloride produces As and AsH_3 (Bettendorff's test).

Arsenious chloride, $AsCl_3$, the chloride of arsenious acid, may be obtained by the action of chlorine on the element, or of hydrochloric acid on arsenious oxide. The latter method of formation suggests that this compound is a salt; and indeed by some of its properties it is thus characterized. It is a colourless liquid, boiling at 130°, and soluble in organic solvents, like other chloranhydrides. It does not immediately give arsenious oxide with water, but first forms the crystalline compound $AsCl(OH)_2$, which may be considered either as a basic salt or a chloroacid. Eventually As_4O_6 separates, and so the following reversible reaction may be recorded:

$$As_4O_6 + 12HCl \rightleftharpoons 4AsCl_3 + 6H_2O.$$

All these considerations are in agreement with those properties of the element arsenic which show it to be more basigenic than phosphorus, and cause it to be classified between the non-metals and metals, as a metalloid.

Arsenious oxychloride, AsOCl, formed as a fuming liquid by the combination of arsenious oxide and chloride, forms $As(OH)_2Cl$ with water.

Antimonious oxide, Sb_4O_6, is a crystalline solid which is isodimorphous with arsenious oxide. It is very slightly soluble in water. The hydroxide, $Sb(OH)_3$, manifests both basic and acidic properties, since it is precipitated from solutions of its salts by alkali hydroxide and redissolved by excess. The hydroxide easily loses water, passing into the crystalline oxide. This behaviour recalls that of arsenious oxide, though arsenious hydroxide has not been obtained, probably because it is not basic enough to be precipitated from solution by alkali.

In addition to orthoantimonious acid, $Sb(OH)_3$, which has been obtained pure, the pyroacid, $Sb_2O(OH)_4$, is likewise known, but the meta-acid, SbOOH, has not been obtained in the free state, although the antimonites correspond to it.

Antimonious oxide would be expected to be more basic

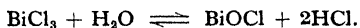
than arsenious oxide. In accordance with this expectation it is found that **antimonious chloride, $SbCl_3$,** is a low-melting solid, soluble in non-hydroxylic solvents, which in the liquid state boils at 223°. It is decomposed by water, forming the solid oxychloride, SbOCl, known as antimonyl chloride, and this when boiled with excess of water yields the oxide. $SbCl_3$ forms various complex salts with the alkali chlorides.

Antimonious bromide is colourless, but the **iodide,** like stannic iodide, is bright red, and forms double salts with alkali iodides, which are of an even deeper colour. The superior basic properties of antimonious oxide are shown in the formation of a crystalline sulphate which separates in needles from a sulphuric-acid solution of Sb_2O_3. A nitrate of somewhat indefinite composition is also known.

Bismuthous oxide, Bi_2O_3, usually occurs as a pale-yellow powder, but when crystalline it is isodimorphous with the two preceding oxides. It is much more basic than antimonious oxide, and indeed possesses no perceptibly acidic properties, since the hydroxide, precipitated from solution by potash or ammonia, is not soluble in excess of alkali.

Bismuthous halides are feeble salts which melt at comparatively low temperatures and can be distilled. Their halanhydride character is shown by their solubility in non-hydroxylic solvents and their formation of complex halacids and alkali salts. Bismuthous iodide, for instance, dissolves in hydriodic acid, forming hydriodobismuthous acid which crystallizes as: $HBiI_4, 4H_2O$. Various types of alkali salts of this acid are known.

The feebly saline character of bismuth halides is manifested by their decomposition by excess of water. Thus the chloride undergoes the following well-known reaction with water, **bismuthyl chloride** being precipitated:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

BiOCl is, however, stable towards water, and thus differs from

SbOCl, which yields the hydrated oxide by further treatment. In this respect bismuth further shows its more metallic character.

The basic nature of bismuthous oxide is best shown by the formation of oxysalts. In addition to the crystalline nitrate, $Bi(NO_3)_3, 5H_2O$, which yields the basic salt $BiONO_3, H_2O$ with water, a basic carbonate, a sulphate, and a phosphate are known. The sulphate forms with potassium sulphate the well-defined double salt $KBi(SO_4)_2$.

A resemblance between antimony and bismuth is shown by the solubility of their hydrated oxides in potassium hydrogen tartrate solution to form emetics, $[K(SbO)C_4H_4O_6]_2H_2O$ and $[K(BiO)C_4H_4O_6]_2H_2O$, which are soluble in water and are therefore the potassium salts of antimonyl- and bismuthyl-tartaric acids.

Sulphides of the Type X_2S_3

The comparison of the sulphides of the elements of a natural group with the corresponding oxides constitutes an important study in chemical analogy, since the progression from acidic to basic functions in the oxides finds a parallel in the corresponding sulphides; and nowhere can this parallel be traced better than in the three elements under consideration.

Arsenious, antimonious, and bismuthous sulphides are all precipitated from slightly acid solutions of their salts by hydrogen sulphide; but whereas the two former sulphides are soluble in dilute alkali hydroxide and sulphide solutions, bismuth sulphide is insoluble in these reagents, just as bismuth oxide is insoluble in alkali. Thus the fact upon which the analytical separation of these elements is based finds an explanation in accordance with the periodic law.

Bismuthous sulphide is, however, somewhat soluble in concentrated sodium-sulphide solution, but is reprecipitated on dilution; unstable compounds of bismuth sulphide with alkalis can also be obtained by fusion.

The reactions which take place in the solution of the above sulphides may be represented as follows:

$$2X_2S_3 + 4KOH = 3KXS_2 + KXO_2 + 2H_2O,$$

or

$$X_2S_3 + 2KSH = 2KXS_2 + H_2S.$$

The analogy between the oxides and sulphides is at once seen. When alkali hydroxide is used to dissolve the sulphide a mixture of thio- and oxysalt is formed; when alkali hydrosulphide is used, thiosalt only results. These sulphides are therefore thioanhydrides which combine with basic sulphides to form metathiosalts.

Whilst bismuth is differentiated from arsenic and antimony by the non-formation of the above compounds, arsenic and antimony may be distinguished, and the more metallic character of the latter manifested, by the following facts: Although arsenic and antimony sulphides are both easily soluble in potassium-hydroxide solution, antimonious sulphide is less soluble than arsenious sulphide in the weaker base, ammonia; and by the use of a still weaker alkali, namely, ammonium carbonate, these two elements may be separated, since whilst arsenious sulphide dissolves in this reagent, antimonious sulphide does not. The method of separation of arsenic and antimony, depending on the insolubility of arsenious sulphide in concentrated hydrochloric acid, also has significance in this connection, since this fact illustrates the greater difficulty with which arsenic assumes basic functions as compared with antimony.

Oxides of the Type X_2O_4

It will be remembered that N_2O_4 is a mixed anhydride forming nitrous and nitric acids with water, and that P_2O_4 similarly forms phosphorous and phosphoric acids. If intermediate oxides are sought among metals, which may present some analogies to this type, they may be found in Fe_3O_4, Pb_3O_4, Mn_3O_4, &c.; and these oxides are salts. With these considerations in view the properties of the tetroxides X_2O_4 may be mentioned.

Arsenic tetroxide or dioxide, As_2O_4 or AsO_2, is said to be formed as a glass when equimolecular proportions of the trioxide and pentoxide are heated together.

Antimony tetroxide, Sb_2O_4.—This oxide, which like Mn_3O_4 is formed when either of the other oxides is strongly heated in the air, is sometimes considered to be antimonious orthoantimonate, $Sb \cdot SbO_4$; it, however, forms the salt $K_2Sb_2O_5$ when fused with potash, and is therefore more probably hypoantimonic anhydride.

Corresponding with Sb_2O_4 are complex salts of the type M_2SbCl_6, derived from the unknown $SbCl_4$.

Bismuth tetroxide, Bi_2O_4, is formed by leading chlorine into boiling potash solution in which Bi_2O_3 is suspended; if too large an excess of potash is present, potassium bismuthate is formed. The compound Bi_2O_4 is perhaps bismuthyl bismuthate, $(BiO)BiO_3$.

Oxides of the Type X_2O_5

The three oxides. As_2O_5, Sb_2O_5, Bi_2O_5, manifest the pro perties of acidic anhydrides, Bi_2O_5 behaving also as a basic peroxide like PbO_2.

Arsenic pentoxide, As_2O_5, resembles phosphoric oxide in dissolving in water to form a strongly-acid solution containing arsenic acid; and it is obtained as a glassy mass by careful ignition of this acid. When strongly heated, unlike phosphorus pentoxide, it breaks up into oxygen and the trioxide, and hence its vapour density has not been determined. Again, whilst phosphorus burns directly to the pentoxide, arsenic produces the trioxide when burnt. Nitrogen pentoxide, prepared by the dehydration of nitric acid, is easily decomposed by heat.

It is therefore seen that the tendency towards complete oxidation, in which phosphorus exceeds nitrogen, and which is so characteristic of the former element, diminishes again with arsenic. Otherwise derivatives of As_2O_5 and P_2O_5 are closely related. Thus the following are among the arsenates and

phosphates which resemble one another in manner of preparation and properties, this resemblance extending to isomorphism in the case of crystalline compounds.

As_2O_5	P_2O_5
NaH_2AsO_4, H_2O	NaH_2PO_4, H_2O
$Na_2HAsO_4, 12H_2O$	$Na_2HPO_4, 12H_2O$
$Na_3AsO_4, 12H_2O$	$Na_3PO_4, 12H_2O$
$MgNH_4AsO_4, 6H_2O$	$MgNH_4PO_4, 6H_2O$
Ag_3AsO_4	Ag_3PO_4
$Na_4As_2O_7$	$Na_4P_2O_7$
$Mg_2As_2O_7$	$Mg_2P_2O_7$
$NaAsO_3$	$NaPO_3$

Unlike the corresponding phosphates, however, meta- and pyroarsenates do not exist in solution, being at once transformed into the orthosalts when dissolved in water.

Moreover, the arsenic acids or hydrated forms of arsenic oxide do not closely resemble the phosphoric acids. It appears that only two forms of solid arsenic acid exist,* viz. $As_2O_5, 4H_2O$, or $2H_3AsO_4, H_2O$, a crystalline solid melting at 36°, obtained by evaporating a solution of As_2O_5 in water until it boils at 150°, and $3As_2O_5, 5H_2O$, or $H_5As_3O_{10}$, or perhaps $3HAsO_3 \cdot H_2O$, prepared from the former by fusion and further loss of water. Thus neither H_3AsO_4, $H_4As_2O_7$, nor $HAsO_3$ appears to exist in the solid state.

Ammonium phosphomolybdate is similar to ammonium arsenimolybdate, though the latter is formed with somewhat more difficulty at a higher temperature than its phosphorus analogue.

Antimony pentoxide, Sb_2O_5, obtained by the gentle ignition of the product of the action of nitric acid on the metal, is a light-yellow powder, practically insoluble in water, though it manifests an acid reaction towards litmus. This oxide is fairly stable, breaking up at high temperature into the tetroxide and oxygen.

Ortho-, pyro-, and meta-antimonic acids are believed to

* Auger, *compt. rend.* (1908), **146**, 585; Balareff, *Zeitsch. anorg. Chem.* (1911), **71**, 73; Menzies and Potter, *J. Amer. Chem. Soc.* (1912), **34**, 1452.

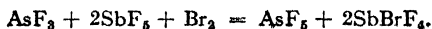
exist. The orthoacid, H_3SbO_4, is obtained by precipitating potassium antimonate with dilute nitric acid, and drying the product over sulphuric acid; the pyroacid, $H_4Sb_2O_7$, is formed by decomposing $SbCl_5$ with hot water and drying the resulting powder at 100°; whilst the meta-acid, $HSbO_3$, is said to result from further heating the pyroacid. Potassium meta-antimonate is known crystalline, and its aqueous solution precipitates from a sodium salt solution $NaSbO_3$, which quickly changes into the crystalline antimonate $Na[Sb(OH)_6]$, the least soluble of sodium salts.

Bismuth pentoxide, Bi_2O_5, is an unstable brown powder obtained by the gentle ignition of bismuthic acid, $HBiO_3$. This latter substance is precipitated as a red powder when chlorine is passed through boiling caustic-potash solution containing bismuthous oxide in suspension; it possesses very feebly acidic properties, as is shown by its method of preparation, and forms unstable salts with alkalis, which are decomposed by water. With hydrochloric or oxyacids it yields bismuthous salts and chlorine or oxygen, thus behaving as a basic peroxide, owing to the instability of bismuthic compounds. It serves to oxidize manganese compounds in acid solution into permanganic acid.

Pentahalides of Arsenic and Antimony

Arsenic and antimony pentafluorides.—It is noteworthy that polyfluorides are much more stable than other corresponding polyhalides, and are vaporized without dissociation. Thus SF_6 and OsF_8 are polyfluorides, to which no other halides correspond. It is interesting therefore to record the existence of arsenic and antimony pentafluorides.

Arsenic pentafluoride, AsF_5, is prepared by the combination of the trifluoride with fluoride, or by the interaction of the trifluoride, antimony pentafluoride, and bromine thus:*

$$AsF_3 + 2SbF_5 + Br_2 = AsF_5 + 2SbBrF_4.$$

* Ruff and Graf, *Ber.* (1906), **39**, 67.

It is a colourless gas to which the salt K_2AsF_7, H_2O corresponds.

Antimony pentafluoride, SbF_5, is a colourless liquid, formed slowly when the pentachloride and anhydrous hydrogen fluoride are boiled together. Bismuth pentafluoride is too unstable to be isolated.

Arsenic and antimony pentachlorides.—It was pointed out when studying phosphorus that phosphorus pentachloride is less stable than the pentoxide, as is manifested in the dissociation of the former by heat. Now since arsenic pentoxide is itself dissociated by heat, it is to be expected that the pentachloride of this element will be very unstable. This is the case, for although $AsCl_5$ is said to be formed by the union of $AsCl_3$ and Cl_2 at $-40°$, the product may be only a solution of chlorine in the trichloride.

Antimony pentoxide, on the other hand, is more stable than arsenic pentoxide, and **antimony pentachloride** is a yellow fuming liquid prepared from the trichloride and chlorine, and sufficiently stable to be distilled under reduced, but not under normal pressure. Its chemical nature may be judged from the fact that it forms a crystallohydrate with ice-cold water, but is decomposed by hot water into antimonic and hydrochloric acids. It thus resembles stannic chloride, just as antimony is comparable with tin in metallic properties.

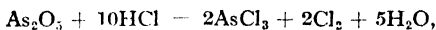
Bismuth pentachloride is not known, and would not be expected to exist, considering the instability of the pentoxide.

PENTASULPHIDES

The pentasulphide of arsenic exists, the existence of that of antimony has been denied, and bismuth pentasulphide is unknown.

Arsenic pentasulphide, As_2S_5, is formed as a yellow precipitate when hydrogen sulphide is passed through a cold solution of an arsenate containing hydrochloric acid. When the proportion of HCl in the solution lies between 7·9 and 14·3

per cent the precipitate consists of As_2S_5 only; if, however, the proportion of the acid is increased the precipitate contains As_2S_3 mixed with sulphur, and when its concentration reaches 32 per cent the precipitate consists of As_2S_3 and sulphur only. The function of the hydrochloric acid appears to be to retard the oxidation of hydrogen sulphide by arsenic acid; but when tne former becomes concentrated it is itself oxidized thus:

$$As_2O_5 + 10HCl = 2AsCl_3 + 2Cl_2 + 5H_2O,$$

so that As_2S_3 is precipitated, accompanied by sulphur formed by the action of chlorine on hydrogen sulphide.* The precipitation of As_2S_5 in the former case is probably preceded by the formation of thioarsenic acids $H_3AsS_nO_{4-n}$, the acid H_3AsS_4 which finally results then decomposing into As_2S_5 and H_2S. As_2S_5 is also formed in the dry way, and may be sublimed. It is a thioanhydride, dissolving in alkalis according to the reaction:

$$As_2S_5 + 6MOH = M_3AsS_4 + M_3AsSO_3 + 3H_2O.$$

In addition to the monothioarsenate, M_3AsSO_3, some dithioarsenate, $M_3AsS_2O_2$, is also formed;† but if alkali sulphide is the solvent, thioarsenate alone results. The free acid is liberated by acidifying a thioarsenate solution, but quickly decomposes, giving a precipitate of the pentasulphide.

Salts of meta- and pyro-, as well as of orthothioarsenic acid, are known.

Antimony pentasulphide.—When hydrogen sulphide is passed through an acidified solution of an antimonate an orange-red precipitate is formed which is supposed to be chiefly Sb_2S_5; and when Sb_2S_3 is boiled with caustic soda and sulphur, the solution after filtering deposits crystals of sodium thioantimonate, Na_3SbS_4, $9H_2O$, known as *Schlippe's salt.* Acid separates from a solution of this salt a precipitate similar to the above. The preparation known as *sulphuret of antimony*, similarly prepared, is said to consist of the pentasulphide

* Usher and Travers, *Chem. Soc. Trans.* (1905), **87**, 1370.
† M'Cay, *Zeitsch. anorg. Chem.* (1900), **25**, 459.

mixed with the trisulphide and sulphur; but according to Kirchhof * Sb_2S_5 does not exist, the precipitate always consisting of **antimony tetrasulphide,** Sb_2S_4, mixed with Sb_2S_3 and sulphur.

THE ELEMENTS OF SUB-GROUP V A

Vanadium, Columbium (Niobium), and Tantalum

Of the elements of this sub-group, vanadium is of interest on account of the number of types of compound which it forms. In this it shows analogy with nitrogen, and especially with phosphorus, although it differs from these elements by reason of its distinctly metallic properties. Columbium and tantalum are rare elements which have some industrial applications.

VANADIUM

This element which occurs in a variety of rare minerals, chiefly as vanadate of lead, was obtained by Roscoe by heating the dichloride in an atmosphere of pure hydrogen. It is a whitish-grey crystalline powder which does not melt nor volatilize when heated to redness in hydrogen. It thus presents a marked contrast to arsenic, its analogue in sub-group V B. Its feebly metallic properties are shown by the fact that it does not displace hydrogen from water or dilute acids except from hydrofluoric acid. It readily absorbs and combines with oxygen and nitrogen when heated in these gases. In small amount it confers tenacity and elasticity upon steel.

Vanadium resembles nitrogen in forming the complete series of oxides, V_2O, $V_2O_2(VO)$, V_2O_3, $V_2O_4(VO_2)$, V_2O_5.

Vanadium monoxide, V_2O, is a neutral oxide, similar to the lower oxides of molybdenum and tungsten, which do not fulfil their expected basic function, being insoluble in acids.

Hypovanadous oxide, V_2O_2, or VO, was mistaken by Berzelius for the metal. A chloride and sulphate are known, the latter forming with potassium sulphate the double salt, $VSO_4, K_2SO_4, 6H_2O$.

* Kirchhof, *Zeitsch. anorg. Chem.* (1920), **112**, 67.

Vanadous oxide, V_2O_3, is insoluble in acids but its chloride and sulphate are well known, the latter forming true alums with alkali sulphates. Vanadyl monochloride, VOCl, is a basic salt.

Hypovanadic oxide, V_2O_4 or VO_2, forms hypovanadates, e.g. $Ag_2V_2O_5$ and $K_2V_4O_9$, $7H_2O$. A tetrachloride is known, and the following basic salts: $VOCl_2$, $V_2O_3Cl_2$, $VO(SO_4)$, $2H_2O$. In this oxide basic and acidic properties are about equal.

Vanadic oxide, V_2O_5, possesses well-developed acidic and feebly basic properties. It is, however, a weak anhydride, and is separated as a red powder from a solution of a salt by addition of acid. This oxide fuses without loss of oxygen. It is used as a catalyst to promote oxidation. Meta- and pyrovanadic acids, and meta- as well as tetra- and hexavanadates exist. These latter salts, which are unrepresented among phosphorus compounds, are peculiarly characteristic of poly-basic acids derived from weak metals or non-metals. Chromium, molybdenum, and tungsten form such poly-acids, as well as boron, among non-metals. Vanadic resembles phosphoric acid in forming complex acids with molybdic and tungstic acids. NH_4VO_3 is the best-known vanadate.

The pentachloride VCl_5 appears not to exist, but $VOCl_3$ is a lemon-yellow liquid, boiling at 126·7°, soluble in non-hydroxylic solvents, and decomposed by water. It is an oxychloranhydride rather than a basic salt.

The sulphate $(VO)_2(SO_4)_3$ may be obtained from a solution of the oxide in concentrated sulphuric acid. It forms double salts with the alkali sulphates.

It will be seen from the above brief account of vanadium compounds that they manifest all stages from basic to acidic properties with increase in proportion of oxygen; but that, in accordance with the position of this element in the A sub-group, even the most highly oxidized derivatives are basic.

Salts corresponding with the various stages of oxidation possess different colours; those of V_2O_5 are yellow, of V_2O_4*

* The lower oxides of vanadium are powerful reducing agents. A solution of V_2O_4 in dilute sulphuric acid serves to standardize permanganate, and after oxidation may be reduced again by SO_2.

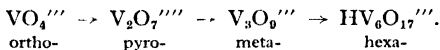
blue, of V_2O_3 green, of V_2O_2 lavender. When zinc is placed in an acidified solution of ammonium vanadate, the above colours may be observed as reduction proceeds. Hydrogen peroxide by oxidizing the solution reverses the colour effects.

The vanadium compounds are here summarized:

VANADIUM COMPOUNDS

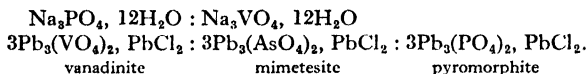
Oxide.	Derivatives.	Colour in Solution.
Vanadium monoxide, V_2O	Neutral oxide, no salts	—
Hypovanadous oxide, VO	VCl_2; VSO_4, $7H_2O$; VSO_4, K_2SO_4, $6H_2O$	Lavender.
Vanadous oxide, V_2O_3	VCl_3 $V_2(SO_4)_3$; $V_2(SO_4)_3$, K_2SO_4, $24H_2O$	Green.
Hypovanadic oxide, VO_2	VCl_4; $VOCl_2$; $VOSO_4$, $2H_2O$ $K_2V_4O_9$, $7H_2O$; $Ag_2V_2O_5$ (hypovanadates)	Blue.
Vanadic oxide, V_2O_5	$VOCl_3$; $(VO)_2(SO_4)_3$ HVO_3; $H_4V_2O_7$; $H_4V_6O_{17}$ (vanadic acids) $NaVO_3$; $Na_4V_2O_7$; $Na_3HV_6O_{17}$, $Na_2H_2V_6O_{17}$ Ag_3VO_4 (by precipitation)	Yellow.

Vanadates differ completely from phosphates in their oxidizing properties. Moreover, the meta-vanadates are stable, whereas the orthophosphates are more stable than the meta- or pyro-salts. Ortho-, meta-, and pyro-vanadates are white or faint yellow, but addition of acid produces orange or red-coloured polyvanadates. These changes may be summarized thus:

$$\underset{\text{ortho-}}{VO_4'''} \rightarrow \underset{\text{pyro-}}{V_2O_7''''} \rightarrow \underset{\text{meta-}}{V_3O_9'''} \rightarrow \underset{\text{hexa-}}{HV_6O_{17}'''}.$$

Further condensation may occur, but finally, hydrated V_2O_5 forms.

Many alkali polyvanadates exist in two forms. The following examples of isomorphism are noteworthy:

$$Na_3PO_4,\ 12H_2O : Na_3VO_4,\ 12H_2O$$

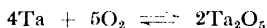
$$\underset{\text{vanadinite}}{3Pb_3(VO_4)_2,\ PbCl_2} : \underset{\text{mimetesite}}{3Pb_3(AsO_4)_2,\ PbCl_2} : \underset{\text{pyromorphite}}{3Pb_3(PO_4)_2,\ PbCl_2}.$$

Because of this isomorphism, vanadium was originally considered a member of sub-group B and not, as now, of sub-group A in series with chromium.

Columbium (Niobium) and Tantalum

In 1801, the English chemist Hatchett reported the existence in an ore of American origin of a new element which he called columbium (Cb). In 1844, Rose, in Germany, announced the discovery of niobium (Nb), which was later shown (1853) to be identical with columbium. This name therefore, has right of priority. Tantalum was discovered in 1802 by Ekeberg.

Columbium is obtained by reducing the pentoxide by " mischmetall " or aluminium; tantalum by reducing K_2TaF_7 by sodium, or by electrolyzing the molten salt.

Both metals are high-melting, lustrous, and stable in air, but combine with oxygen on heating. The reaction

$$4Ta + 5O_2 \rightleftharpoons 2Ta_2O_5$$

is reversible in vacuo at high temperature, and serves to produce the pure metal, which thus shows analogy with the metals of Group VIII.

They are soluble in hydrofluoric acid only, and with fused alkalis yield columbates and tantalates.

Use has been made of both elements in electrolytic rectifiers of alternating current. Tantalum was used for incandescent electric filaments prior to its displacement by tungsten.

The following **oxides** have been reported; CbO (doubtful); Cb_2O_3; CbO_2; Cb_2O_5; TaO_2; Ta_2O_5.

Simple divalent salts are unknown. Reduction of $CbCl_5$ by sodium or lead gives the green complex **chlorocolumbium chloride,** probably $H[Cb_3Cl_7 . H_2O]3H_2O$. Tantalum forms similar chloro- and bromo- compounds, in which one of the halogen atoms is replaceable by Br′, OH′ or SO_4'', giving, for example, $H[Ta_3Cl_6 . Br . H_2O]3H_2O$. These complexes (which occur also with molybdenum and tungsten) indicate very weak saline power in the bivalent state.

Columbium sesquioxide, Cb_2O_3, and the **dioxide,** CbO_2 are obtained by reducing Cb_2O_5 by magnesium or hydrogen. **Tantalum dioxide,** TaO_2, is similarly prepared using mag-

nesium. Neither dioxide shows basic properties towards acids, and with alkali they yield columbates and tantalates. The chlorides, $CbCl_3$ (black), and $TaCl_3$ (green), have been isolated, but tetrachlorides are doubtful.

These tervalent chlorides show saline character in their stability towards water, $CbCl_3$ not being attacked, and $TaCl_3$ but slowly (cf. $CrCl_3$); hence tervalent columbium is apparently the more basigenic. Both oxidize readily. By means of zinc in acid solution, columbates, but not tantalates, may be reduced with colour change to the tervalent stage.

The **pentoxides,** Cb_2O_5, Ta_2O_5, are obtained by drying the gelatinous precipitates obtained by hydrolysis of the pentahalides, or by the action of acids on columbates or fluoxycolumbates and tantalates or fluotantalates.

The oxides are white powders, soluble, after ignition, in HF only. Ta_2O_5 is remarkably stable. Unlike Cb_2O_5, it is not attacked by CCl_4 alone, nor reduced by hydrogen. When fused with alkalis, columbates and tantalates are formed. These salts, which are generally insoluble and complex, are analogous to the vanadates. The hypothetical acid, H_3TaO_4, is represented in $K_7[Ta(TaO_4)_4]12H_2O$, a member of a series which contains the only known soluble alkali tantalates.

True columbic and tantalic acids are unknown, the products obtained by the action of acids on their salts being hydrous oxides of marked colloidal character, resembling silicic, titanic, and zirconic acids. The pentoxides are thus weak acidic anhydrides; Ta_2O_5 being slightly more basic, since tantalates are decomposed more readily than columbates by dilute acetic acid or carbon dioxide. The close resemblance of columbium and tantalum in their compounds is due probably to the lanthanide contraction (q.v.), though the difference here is more marked than with zirconium and hafnium.

The power to form heteropolyacids, so marked in vanadium, is very limited here.

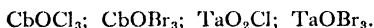
As with vanadium, per-salts result by the action of hydrogen peroxide on alkali columbates and tantalates. The per-acids

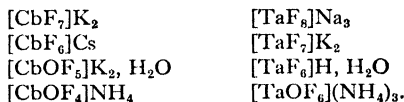
are of the type HMO_4, xH_2O; pervanadic acid is unstable, pertantalic acid is stable at 100°, and gives no hydrogen peroxide with cold dilute sulphuric acid.

With the exception of CbI_5, all the **pentahalides** MX_5, are known. The existence of TaI_5, in which the member of highest atomic number exhibits the group valency towards iodine, is remarkable in this section of the periodic table.

These halides may be obtained in the dry-way only, by the action of halogens on the metal or on a mixture of oxide and carbon. TaF_5 is also formed by the action of dry HF on $TaCl_5$; similarly $TaBr_3$ and HI yield TaI_5. They are halanhydrides, readily volatile, and hydrolyzed at once by water.

Oxyhalides are known, but they are oxy-halanhydrides, forming no salts of the uranyl type. Some examples are:

$CbOCl_3$; $CbOBr_3$; TaO_2Cl; $TaOBr_3$.

Fluoxy- and fluo-columbates and tantalates.—The separation of columbium and tantalum was first achieved by Marignac (1866) by dissolving the mixed pentoxides in concentrated HF, adding potassium fluoride and concentrating carefully. He thus obtained **potassium fluoxycolumbate**, $K_2[CbOF_5]H_2O$ and **potassium fluotantalate** (or tantalifluoride), K_2TaF_7. This latter being least soluble, and the two substances not being isomorphous, a separation was effected. Some examples of these numerous complex compounds are:

$[CbF_7]K_2$	$[TaF_8]Na_3$
$[CbF_6]Cs$	$[TaF_7]K_2$
$[CbOF_5]K_2$, H_2O	$[TaF_6]H$, H_2O
$[CbOF_4]NH_4$	$[TaOF_6](NH_4)_3$.

Fluoxytantalates do not form when HF is present; fluoxycolumbates may form, but excess HF produces fluocolumbates.

The **sulphide,** TaS_2, results when a mixture of H_2S and

CS_2 is passed over heated Ta_2O_5. The black powder is stable to hot HCl. Columbium disulphide is doubtful.

NOTE ON THE FIXATION OF ATMOSPHERIC NITROGEN

A study of the distribution of terrestrial nitrogen shows that this element is present in volcanic gases, and that it exists combined in small quantities in deep-seated nitrides and in surface deposits of nitrates, as well as in accumulations of nitrogenous matter of undoubtedly organic origin. Thus nitrogen appears to form but a very small part of the crust or internal mass of the earth.

This fact is no doubt to be attributed to the inertness of nitrogen, which consequently failed to combine to any extent with other elements in the earlier stages of cosmic development. Some of this free cosmic nitrogen was probably originally occluded within the generating material of our planet, and eventually accumulated outside the earth, forming the larger part of our atmosphere.

Notwithstanding the comparative rarity of combined nitrogen, this element plays an essential part in vegetable and animal metabolism, since it enters into the composition of the numerous and important class of proteins.

How nitrogen has become available for plant and animal life, and how its availability may be increased artificially, are questions which will here be dealt with.

Plants require nitrogenous food in the form of soluble nitrate; and this material results naturally from atmospheric electric discharge, whereby nitric acid is formed. In this way about eleven pounds of nitrate per acre are annually formed in the temperate, and a larger amount in the tropical regions. This, however, is not the only means by which atmospheric nitrogen is fixed.*

* According to B. Moore, both lower and higher plants build up nitrates and nitrites, and form organic nitrogen compounds, from the free nitrogen of the atmosphere (*Chem. Soc. Trans.* (1921), **119**, 1565).

Nodules found on the roots of leguminous plants consist of colonies of **azoto bacteria**, which in symbiotic union with these plants enable them directly to assimilate atmospheric nitrogen.

Rotation of crops, justified by long experience, depends on the enrichment of exhausted soil by a leguminous crop.

Thus, firstly by electric discharge, and secondly by the aid of certain micro-organisms, atmospheric nitrogen is made available for plant, and thence for animal food.

Simultaneously, however, some nitrogen is being yielded back to the air by organic decay, and the work of denitrifying bacteria; but the currency of most of the fixed nitrogen is upheld through the agency of **nitrifying bacteria.**

Animal waste nitrogen is eliminated chiefly in the form of urea, of which it has been calculated that about 40,000 tons per day are produced by mankind alone. In the soil urea is hydrolyzed to ammonium carbonate, and the ammonia of this salt is converted first to nitrite and eventually to nitrate by nitrifying bacteria. This is a natural process, which is employed and can be followed readily in the course of sewage purification. Nitrates are the final products of natural purification, and are also the most available nitrogenous plant foods.

Under conditions of artificial cultivation, but especially by reason of sewage disposal systems rendered necessary by the congestion of population, animal nitrogenous waste is very largely diverted from the soil to the sea. This is perhaps the most serious cause of depletion of the soil of nitrogen; for unless nearly all the animal waste resulting from the use of nitrogenous vegetable food is returned to the soil, local impoverishment must occur. It thus becomes needful to supply nitrogenous manures, of which the main sources are:

(*a*) Guano, which is limited in quantity, is not the most available form, and is practically exhausted.

(*b*) Ammonia in the form of sulphate, derived from the destructive distillation of shale and coal.

(*c*) Chile saltpetre, or sodium nitrate.

The world production of sulphate of ammonia in 1920 was 2,015,000 tons, and of Chile saltpetre 2,966,000 tons, but owing to war requirements a somewhat higher maximum of saltpetre exportation had been reached in 1917.

The question of the early exhaustion of the Chilean deposits has been raised, and the anticipation of a world shortage of nitrogenous manures has stimulated the artificial fixation of nitrogen; but it is estimated that at the present rate of production the nitrate beds will certainly last for another 200 years (Hobsbaum and Grigioni, *J. Soc. Chem. Ind.* (1917), **36**, 62) Nevertheless the artificial production of nitrogen compounds has so increased during recent years that it now exceeds in amount the annual yield of natural nitrate, as the following figures show:

Product.	Production in Percentages.			
	1912		1920	
Chile nitrate		57·5		30·2
By-product ammonium sulphate		38·0		26·6
Fixation products:				
Cyanamide	3·1		20·9	
Nitrate of lime ..	1·4		2·5	
Synthetic ammonia	nil		19·8	
Total fixation products		4·5		43·2
		100·0		100·0

The proportions of the total fixed nitrogen obtained artificially had been as follows in some previous years:

1909, 1 per cent; 1913, 10 per cent; 1917, 30 per cent.*

In the atmosphere there are about 4000 billion tons of nitrogen; or otherwise, over 1000 acres there is nitrogen equivalent to nearly 200 millions of tons of Chile saltpetre. Yet by reason of the relative inertness of nitrogen the

* *J. Soc. Chem. Ind.* (1921), **40**, 285R.

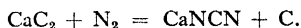
problem of fixing this element by chemical methods at a price to compete with ammonia and saltpetre has been one of great difficulty.

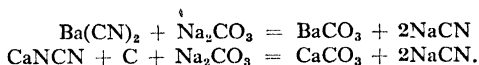
The chemical fixation of atmospheric nitrogen can be carried out most economically where a natural head of water affords cheap motive power. Such source of power is not, however, essential. The processes employed, as indicated above, are three: (i) the formation of calcium cyanamide, CaNCN, by absorption of nitrogen by calcium carbide; (ii) the formation of nitric oxide, subsequently converted into nitric acid, by the action of the electric arc on air; (iii) the synthesis of ammonia from its elements, and the subsequent oxidation of this compound to nitric acid.

The Cyanamide Process.—The union of acetylene and nitrogen to form hydrocyanic acid was demonstrated by Berthelot in 1869. Carbides of barium and calcium, whose preparation we owe to Moissan, similarly unite with nitrogen at high temperatures, but only when impure, to yield in the case of barium a mixture of cyanide and cyanamide:

$$BaC_2 + N_2 = Ba(CN)_2$$
$$BaC_2 + N_2 = BaNCN + C,$$

and in the case of calcium, cyanamide only:

$$CaC_2 + N_2 = CaNCN + C.$$

Each of these derivatives yields sodium cyanide, and the alkaline-earth carbonate, on fusion with sodium carbonate:

$$Ba(CN)_2 + Na_2CO_3 = BaCO_3 + 2NaCN$$
$$CaNCN + C + Na_2CO_3 = CaCO_3 + 2NaCN.$$

Under the names of " calcium cyanamide ", " kalkstickstoff ", or " nitrolim ", the calcium compound is now produced commercially.

The preparation of " nitrolim " requires pure nitrogen. In the factories at Odda, in Norway, atmospheric nitrogen is separated from the air by means of a Linde liquefying plant,

advantage being taken of the boiling-point difference between nitrogen, $= -196°$ C., and oxygen, $= -183°$ C.

As alternative processes for obtaining nitrogen, air may be passed over hot copper, the oxide being subsequently reduced by generator gas; or producer gas (N_2, CO, O_2) may be passed over a hot mixture of copper and its oxide, whereby a mixture of nitrogen and carbon dioxide is formed (Caro).

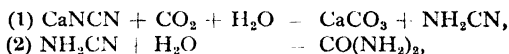
The reaction of formation of calcium cyanamide,

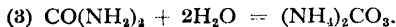
$$CaC_2 + N_2 \rightleftharpoons CaNCN + C,$$

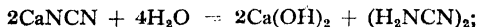
begins at 800° to 900° C., and is reversible above 1000° C. Admixture of calcium chloride or fluoride facilitates the reaction, probably by lowering the fusion temperature.

The use of cyanamide as a fertilizer depends on the formation by hydrolysis of ammonia, which is eventually converted into nitrate by the nitrifying organisms of the soil.

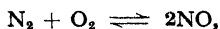
The former reactions probably are:

$$(1)\ CaNCN + CO_2 + H_2O = CaCO_3 + NH_2CN,$$
$$(2)\ NH_2CN + H_2O = CO(NH_2)_2,$$

the urea thus formed being hydrolyzed (by the hydrolytic micrococcus of urea) to ammonium carbonate:

$$(3)\ CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

Other applications of nitrolim are: the formation of ammonia by means of superheated steam; the formation of cyanides, $CaNCN + C \rightleftharpoons Ca(CN)_2$, by heating with a suitable flux; the formation of dicyandiamide by the action of cold water,

$$2CaNCN + 4H_2O = 2Ca(OH)_2 + (H_2NCN)_2;$$

and the production of urea, $CO(NH_2)_2$ of guanidine, $HN : C(NH_2)_2$, and of nitroguanidine, $NO_2N : C(NH_2)_2$, by the action of acids.

The Atmospheric Nitric Acid Process.—The direct union of oxygen and nitrogen with the formation of nitric oxide, in accordance with the reversible reaction:

$$N_2 + O_2 \rightleftharpoons 2NO,$$

either under the influence of the electric discharge, or at the temperature of a hot flame such as that of hydrogen, has long been known, having first been observed by Priestley and by Cavendish.

Nitric oxide is endothermic, and unstable above 1200°; at 3200° about 5 per cent by volume can be formed from air, and about 14 per cent from an equimolecular mixture of oxygen and nitrogen. Owing, however, to the difficulty of rapidly cooling the gases from the temperature of the electric arc (about 3000° to 3500°) to below the stability temperature (1200°), the actual yields of oxide do not exceed 1·5 to 2 per cent of the volume of air employed.

In the design of a nitrogen fixation furnace the following points have to be considered.*

(i) To insure that as much of the air as possible is brought into contact with the arc flames.

(ii) To remove quickly and cool the nitric oxide formed.

It is important also to provide for automatic regulation of the current and continuity of working.

The electrodes are made of metal, generally of an alloy of copper or aluminium, but sometimes of steel; they are hollow so as to be water-cooled. The entering air is sometimes preheated by the waste heat of the furnace, and it is advantageous to use a mixture of nitrogen and oxygen in equal volumes instead of air; the yield, also, is increased if the temperature of the arc can be raised from 3200° to 4200° C.

The chief types of furnace are:

(*a*) magnetically-blown arc furnace (Birkeland-Eyde);
(*b*) air-blown arc furnace (Pauling);
(*c*) longitudinal standing arc furnace (Schönherr-Hessberger)
(*d*) three-phase furnace (Kilburn Scott).

Alternating currents of high potential are used in all these furnaces. In the Birkeland-Eyde (Scandinavian) furnace the arc oscillates rapidly in an electro-magnetic field, as the current

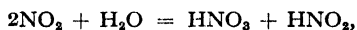
* E. Kilburn Scott, *J. Soc. Chem. Ind.* (1915), **34**, 113; (1917), **36**, 771.

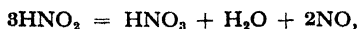
alternates, producing the appearance of a disc of flame. The nitric oxide is thus swept forwards by a continuous current of air without the decomposition it would suffer if the arc occupied one position continuously.

In the Pauling furnace the nitric oxide is carried away from the zone of production by an air blast instead of by electro-magnetic action, whilst in the Schönherr-Hessberger furnace the arc is drawn up a narrow tube by a whirling current of air, and so the dissociation of the nitric oxide is prevented, whilst the incoming air is preheated by the heat of the escaping air.

The furnace of Kilburn Scott, devised for use in Great Britain, differs from the above in the employment of the three-phase alternating current. The reaction chamber is in the shape of an inverted hexagonal cone the faces of which consist alternately of the alloy composing the three electrodes and of firebricks. Inside this chamber the three-phase arc flame rotates fifty times a second, and through it the air, preheated to 250° C., passes upwards from a nozzle at the base. Since the air takes more than $\frac{1}{50}$ second to pass through the furnace, all of it necessarily comes into contact with the flame. At the top of the furnace is a boiler on which the issuing gas impinges; and, since nitric oxide has no action on metals, this boiler is not corroded provided the temperature of the gas is not lower than 600° C., below which temperature NO_2 is formed. Thus the cooling of the gas furnishes heat for power production.

When the gases, finally cooled to about 50° C., react with water a mixture of nitric and nitrous acids is formed:

$$2NO_2 + H_2O = HNO_3 + HNO_2,$$

but nitrous acid rather easily undergoes self-oxidation and reduction, especially in higher concentration, thus:

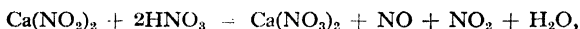
$$3HNO_2 = HNO_3 + H_2O + 2NO,$$

and the nitric oxide with a fresh quantity of oxygen again

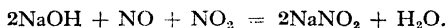
yields NO_2, so that the greater part of the peroxide is converted eventually into nitric acid.

Absorption is effected in a series of towers in which the water passes in the opposite direction to the gas current, so that acid of about 50 per cent strength is formed in the first tower, whilst nitrous acid tends to be formed in the last. An additional tower, containing milk of lime, effects the removal of the last traces of oxides, in the form of calcium nitrite and a little nitrate.

The acid may be concentrated by distillation with sulphuric acid, or it may be neutralized with chalk and the solution evaporated till crystallized calcium nitrate, $Ca(NO_3)_2, 4H_2O$, separates; or the liquid may be still further concentrated until it sets to a hard mass, forming the " Norwegian saltpetre " or " air saltpetre " of commerce.

Nitrites are obtained from the product in the last tower. If calcium nitrite has been made, " nitrous fumes " are produced by the action of nitric acid:

$$Ca(NO_2)_2 + 2HNO_3 = Ca(NO_3)_2 + NO + NO_2 + H_2O,$$

and on absorption by caustic soda give technically pure nitrite,

$$2NaOH + NO + NO_2 = 2NaNO_2 + H_2O.$$

The Synthesis and Oxidation of Ammonia.*—It has long been known that when a mixture of nitrogen and hydrogen is led over a catalyst such as iron or manganese, small amounts of ammonia are produced. It was discovered by Haber that by greatly increasing the pressure on the gases, and maintaining the temperature of the catalyst at 600° C., the yield of ammonia could be so increased that the commercial synthesis of this product became practicable. Ammonia can then be oxidized in presence of a catalyst to nitric acid, whence ammonium and sodium nitrates are prepared. Thus, in 1916, 400,000 tons of atmospheric nitrogen were converted

* Maxted, *J. Soc. Chem. Ind.* (1917), **36**, 777; Partington, *J. Soc. Chem. Ind.* (1921), **40**, (R) 99, 144, 185.

into synthetic products in Germany, so that the importation of Chile saltpetre became unnecessary.

For successful working the gases employed must reach a high state of purity. Pure nitrogen can be obtained by liquefying air, and pure hydrogen by electrolysis. The former process is, however, only supplementary, and the latter is too expensive. Methods of purification have been so perfected that pure nitrogen and hydrogen can be obtained from a mixture of producer gas and water gas of the following percentage composition: 40 per cent H_2, 30 per cent CO, 12 per cent CO_2, 18 per cent N_2.

Carbon monoxide is eliminated by causing the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ to take place in presence of a catalyst. The carbon dioxide is then removed from the gaseous mixture by absorption in water under pressure, and the remaining carbon monoxide by exposure to concentrated sodium hydroxide solution at high temperature and pressure so that sodium formate is produced. The remaining gases, brought exactly to the proportion $N_2 : 3H_2$ by the addition of nitrogen made from air by the Linde liquefaction process, and under a pressure of 200 atmospheres, are passed over the catalyst consisting of iron with an activator (possibly molybdenum) at 600° C., and the ammonia produced is dissolved in water under the same pressure, or liquefied in a refrigerator.

The oxidation of ammonia to nitric acid in presence of a metallic catalyst, discovered by Kühlmann in 1830, was developed into a commercial process by Ostwald in 1902. Base metal catalysts, such as iron, activated with bismuth, copper, &c., may replace platinum, and when the mixture of ammonia and air is passed over the catalyst at 700° C. at such a velocity that the period of contact is 0·03 second or less, decomposition of the oxides of nitrogen formed is prevented, and 90 per cent of the ammonia is converted into nitric acid. The oxidation proceeds according to the reaction:

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

Such are the purely chemical methods by which the problem of the fixation of nitrogen has been solved. Attempts to find a solution on biological lines, by application to the soil of pure cultures of the nitrogen-assimilating organism, have been numerous, but are of secondary importance.

NOTE ON LIQUID AMMONIA AS A SOLVENT

In various reactions ammonia is analogous to water, as in the formation of alkali and acidic amides from alkali metals and acidic chlorides respectively, as well as of imides from the amides of dibasic organic acids by loss of ammonia. Thus it is suggested that the amide group ($'NH_2$) is analogous to hydroxyl ('OH), whilst the imide group ("NH) is analogous to oxide ("O).

This analogy may be further developed.

OH attached to metal gives an oxybase, e.g. KOH,
NH_2 attached to metal gives an **ammonobase**, e.g. KNH_2,
OH attached to an acidic group gives an oxyacid, e.g. R·COOH,
NH_2 attached to an acidic group gives an **ammonoacid**, e.g. $R \cdot CO \cdot NH_2$.

Hence the following reactions are analogous:

$$KOH + R \cdot CO \cdot OH \rightleftharpoons R \cdot CO \cdot OK + HOH$$
$$KNH_2 + R \cdot CO \cdot NH_2 \rightleftharpoons R \cdot CO \cdot NHK + NH_3;$$

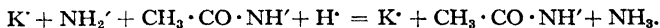
that is to say, analogous to oxysalt formation and hydrolysis there are **ammonosalt formation** and **ammonolysis**. Just as the oxy-reactions are realizable through the agency and medium of liquid water, so the analogous ammono-reactions take place in liquid ammonia; this has been shown by Franklin and his co-workers, to whom both the reactions and the nomenclature are due.*

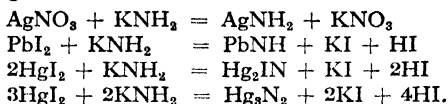
Anhydrous liquid ammonia, which boils at −33·3°, resembles water in being itself a non-electrolyte, and a good solvent and ionizing medium.

If potassamide is dissolved in liquid ammonia containing phenolphthalein, the colourless liquid turns red owing to

* *J. Amer. Chem. Soc.* (1905), **27**, 820–51.

the presence of alkali. The ammonobase KNH_2 has been ionized, and the alkalinity must be due to NH_2 ions. The colour of the indicator is discharged by the addition of acetamide, $CH_3 \cdot CO \cdot NH_2$, an ammonoacid, whose H ions unite with NH_2 ions to produce ammonia, which becomes part of the solvent, thus:

$$K^{\cdot} + NH_2{}' + CH_3 \cdot CO \cdot NH' + H^{\cdot} = K^{\cdot} + CH_3 \cdot CO \cdot NH' + NH_3.$$

Reactions of precipitation can also be carried out in the same medium, e.g.

$$AgNO_3 + KNH_2 = AgNH_2 + KNO_3$$
$$PbI_2 + KNH_2 = PbNH + KI + HI$$
$$2HgI_2 + KNH_2 = Hg_2IN + KI + 2HI$$
$$3HgI_2 + 2KNH_2 = Hg_3N_2 + 2KI + 4HI.$$

Silver amide, $AgNH_2$, and lead imide, PbNH, are new substances; the nitrogenous mercury compounds have been obtained in other ways (see p. 203).

CHAPTER X

GROUP VI

SUB-GROUP A		SUB-GROUP B
	8 O (16·00)	
	16 S (32·06)	
24 Cr (52·0)		34 Se (79·2)
42 Mo (96·0)		52 Te (127·5)
74 W (184·0)		84 Po
92 U (238·2)		

The sub-groups VI A and VI B respectively form families of closely related elements, in both of which the change of chemical character is from less to more basigenic. Whilst the members of sub-group B are acid-producing, signs of a basic character first appearing in tellurium, the elements of the A sub-group are base-producing or metallic, acidic characters being displayed only in compounds containing a large propor-

tion of a non-metallic element, such as the trioxides, MO_3, which show acidic properties, diminishing in degree from chromium to uranium.

As would be expected, from principles of the periodic law previously considered, the relationship between sub-groups A and B is somewhat remote; but the maintenance of the group type by the formation of a series of acidic trioxides clearly reveals a similarity that justifies the inclusion of all these elements in one group. As in the case of other groups, hydrides and volatile alkyl compounds are formed only by the members of the B sub-group.

The maximum halogen valency of Group VI is six, the type being represented, however, only by MoF_6, WF_6, WCl_6, and SF_6. Other halogen valencies, 2, 3, 4, and 5, are all represented. The oxygen valency is also six, and is represented by the highest normal oxides, MO_3.

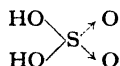
The electronic structures assigned to some representative atoms of Group VI are as follows:

O	2	2.4					
S	2	8	2.4				
Te	2	8	18	18	2.4		
Cr	2	8	2.2.4.5	1			
W	2	8	18	32	2.2.4.4	2	
U	2	8	18	32	18	2.2.4.5	1.

In every case the exercise of the group valency requires the atom to contribute six electrons in its valency group. The transition elements in sub-group VI A achieve this by transferring the necessary electrons from the next quantum group. The hexahalides are 6-covalent, the inner quantum groups containing 2, 8, 18 or 32 electrons, and the valency group, 12 electrons, the additional 6 electrons being derived from the halogen atoms. Thus, for tungsten in WCl_6 the structure is 2 . 8 . 18 . 32 . 8 . 6 $(6)^{\swarrow}$, the sign $(^{\swarrow})$ signifying the number of electrons to be added.

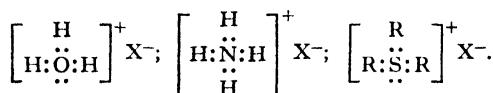
The addition of two electrons to the six already present

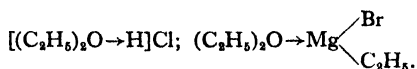
produces a stable octet, which exists when the element forms the characteristic acids, H_2MO_4, e.g.,

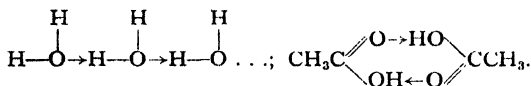
$$\begin{matrix} HO \\ HO \end{matrix} \!\!>\! S \!\!\begin{matrix} \nearrow O \\ \searrow O \end{matrix}$$

The non-existence of H_4SO_5 and H_6SO_6, indicates that sulphur cannot increase the octet to accommodate more oxygen atoms, although telluric acid, H_2TeO_4, $2H_2O$ is most probably $Te(OH)_6$. Hydrates, such as H_2SO_4, H_2O and H_2SO_4, $4H_2O$, arise in another way.

In the highly oxidized compounds given by hydrogen peroxide the valency of the central atom is still presumably six, if the formulæ for the perchromic acids given within are accepted. It seems to be a general rule that the formation of per-acids and per-salts does not cause any change in the valency of the central atom.

Oxygen is generally bivalent, since its 6 electrons become 8 in combination. Nevertheless, in bivalent union, an oxygen atom possesses two lone pairs of electrons, to which other atoms may be co-ordinated. Hence, when acids dissolve in water, oxonium salts, analogous to ammonium and sulphonium salts, are believed to form, thus:

$$\left[\begin{matrix} & H & \\ H: & \ddot{\underset{\cdot\cdot}{O}} & :H \end{matrix}\right]^+ X^-; \quad \left[\begin{matrix} & H & \\ H: & \ddot{\underset{\cdot\cdot}{N}} & :H \\ & H & \end{matrix}\right]^+ X^-; \quad \left[\begin{matrix} & R & \\ R: & \ddot{\underset{\cdot\cdot}{S}} & :R \end{matrix}\right]^+ X^-.$$

Aqueous hydrogen chloride is thus $[OH_3]^+Cl^-$, oxonium chloride, and oxygen is 3-covalent. The same tendency is evident in the formation of salts of ethers and ketones, in chelate compounds (q.v.), and in the Grignard compounds:

$$[(C_2H_5)_2O \rightarrow H]Cl; \quad (C_2H_5)_2O \rightarrow Mg \begin{matrix} \diagup Br \\ \diagdown C_2H_5. \end{matrix}$$

The association of water or alcohols, and the existence of double acetic acid molecules may have the same cause, thus:

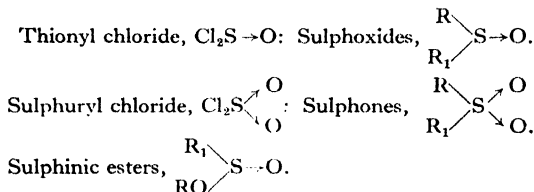
$$H{-}\overset{\overset{H}{|}}{O}{\rightarrow}H{-}\overset{\overset{H}{|}}{O}{\rightarrow}H{-}\overset{\overset{H}{|}}{O} \ldots; \quad CH_3C\begin{matrix}{\nearrow\!\!\!\!/}O{\rightarrow}HO{\searrow}\\{\searrow}OH{\leftarrow}O{\nearrow\!\!\!\!/}\end{matrix}CCH_3.$$

Oxygen in the 4-covalent state exists in basic beryllium acetate (q.v.).

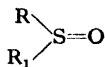
Oxygen thus appears to possess basic properties, and water itself is a base, being, on the Lowry-Brönsted definition, an acceptor of hydrogen ions, though in the majority of its combinations oxygen confers acidic properties, the higher oxides of an element, for example, being generally more acidic than the lower.

Sulphur shows a covalency of two in H_2S, but, unlike H_2O, this compound does not appear to be associated. In the compounds listed below, the sulphur atom has a completed octet, the molecules containing co-ordinate links.

Thionyl chloride, $Cl_2S{\rightarrow}O$: Sulphoxides, $\begin{matrix}R\searrow\\R_1\nearrow\end{matrix}S{\rightarrow}O.$

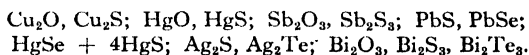
Sulphuryl chloride, $Cl_2S\begin{matrix}\nearrow O\\\searrow O\end{matrix}$: Sulphones, $\begin{matrix}R\searrow\\R_1\nearrow\end{matrix}S\begin{matrix}\nearrow O\\\searrow O.\end{matrix}$

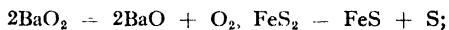
Sulphinic esters, $\begin{matrix}R_1\searrow\\RO\nearrow\end{matrix}S{\rightarrow}O.$

These structures arise from parachor measurements (Sugden, 1925, 1926), and from the notable fact that alkyl sulphoxides and sulphinic esters both form optically active isomers (Phillips, 1925, 1926). The necessary molecular asymmetry can only arise if these active compounds possess one co-ordinate bond, for the structure

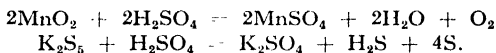
$$\begin{matrix}R\searrow\\R_1\nearrow\end{matrix}S{=}O$$

would be planar and no activity is possible. The actual structure is tetrahedral, the unused electron pair of the sulphur atom being towards the apex.

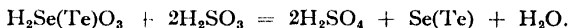
SUB-GROUP VI B

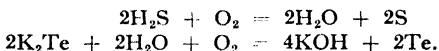
Oxygen, sulphur, selenium, and tellurium all form binary compounds with metals from which acids liberate the hydrides H_2X. The occurrence of these elements in nature in the form of such metallic compounds illustrates the analogy between them, for example:

$$Cu_2O,\ Cu_2S;\ HgO,\ HgS;\ Sb_2O_3,\ Sb_2S_3;\ PbS,\ PbSe;$$
$$HgSe + 4HgS;\ Ag_2S,\ Ag_2Te;\ Bi_2O_3,\ Bi_2S_3,\ Bi_2Te_3.$$

A comparable mode of preparation of the elements is furnished by the decomposition of the hydrides either by heat or, in the case of oxygen, by electrolysis. Other comparable methods for oxygen and sulphur are the heating of the higher oxides or sulphides, as, for example:

$$2BaO_2 = 2BaO + O_2,\ FeS_2 = FeS + S;$$

and the decomposition of similar compounds by acids, e.g.:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$
$$K_2S_5 + H_2SO_4 = K_2SO_4 + H_2S + 4S.$$

Selenium and tellurium result from the reduction of selenious and tellurious acids by sulphurous acid:

$$H_2Se(Te)O_3 + 2H_2SO_3 = 2H_2SO_4 + Se(Te) + H_2O.$$

Selenium, tellurium, and sulphur are liberated when their hydrides or metallic compounds are decomposed by oxygen:

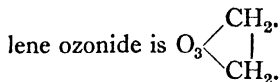
$$2H_2S + O_2 = 2H_2O + 2S$$
$$2K_2Te + 2H_2O + O_2 = 4KOH + 2Te.$$

All these elements show *allotropy*.

Allotropy of Oxygen

Besides ozone, allotropic forms of solid oxygen exist.

Ozone is formed from oxygen with absorption of 34,500 calories when disruption of O_2 molecules takes place under conditions favouring condensation to O_3 molecules.

In the electrolysis of dilute H_2SO_4 with a minute anode of platinum foil, the evolved oxygen may contain 23 per cent of

ozone;* and when a silent discharge is passed through oxygen at the temperature of liquid air, 99 per cent of the gas is converted into ozone.† The stability of ozone diminishes with rise of temperature, and at 300° it is completely reconverted into oxygen. Ozone differs from hydrogen peroxide, which otherwise, as an oxidizing agent, it much resembles, in not reacting with chromic acid. It combines with certain unsaturated organic compounds, e.g. turpentine, to form ozonides. Ethylene ozonide is $O_3\left<\begin{matrix}CH_2.\\ |\\ CH_2.\end{matrix}\right.$

PHYSICAL PROPERTIES OF OXYGEN AND OZONE

	M.P.	B.P.(1 atm.).	Colour of Liquid	Magnetic Properties	Solubility in 1 Vol. Water at 0°.
Oxygen, O_2	−219°	−182·5°	Pale-blue.	Strongly magnetic	0 0489
Ozone, O_3 . .	−249·7°	−119°	Indigo-blue.	„	0 01

ALLOTROPY OF SULPHUR

Sulphur presents a complicated case of allotropy.

Rhombic sulphur, S_α, crystallized from carbon disulphide solution by spontaneous evaporation, has a density at 0° of 2·06 and melts at 112·8°; it is the most stable form of sulphur at atmospheric temperature, into which all the other forms pass on keeping. It is therefore the form in which sulphur occurs naturally.

Monoclinic sulphur, S_β, formed by the crystallization of the molten element near its melting-point, has a density of 1·96, and melts at 119·25°; it passes into the rhombic form below 96°, which is the transition temperature of these two allotropic forms. The change, which is enantiotropic, is represented thus:

$$S_\alpha \overset{96°}{\rightleftharpoons} S_\beta$$

* Fischer and Bendixsohn, *Zeit. anorg. Chem.*, 1909, **61**, 13.
† Briner and Durand, *Comp. rend.*, 1907, **145**, 1272.

Two other varieties of monoclinic sulphur exist, being known respectively as *tabular sulphur*, formed by the superficial oxidation of an alcoholic solution of sodium polysulphide, and *nacreous sulphur*, formed by cooling in a freezing mixture a solution obtained by heating sulphur with benzene or other solvent in a sealed tube.

It is well known that when sulphur is melted, and then further heated, it changes from a yellow, mobile liquid to a dark red viscous liquid, and then, before boiling, to a liquid which is almost black, but again mobile. These phenomena are due to the existence of two forms of liquid sulphur, known respectively as S_λ and S_μ, as well as to another form,* solid when isolated, known as S_π. The change of viscosity of molten sulphur as the temperature is raised is believed to be due to the formation of S_π from S_λ. Plastic sulphur, formed by suddenly cooling molten sulphur from near its boiling-point, consists of about 99 per cent S_μ and 1 per cent S_λ.

Soon after it has been melted the solidifying point of sulphur is 119·25°. This is the freezing-point of S_λ, or the melting-point of S_β, into which molten sulphur first passes on solidifying. But when molten sulphur is kept for some hours at a temperature just above its melting-point its solidifying-point falls to 114·5°. This change is due to the transformation of some of the S_λ into S_π. Both rhombic (S_α) and monoclinic (S_β) sulphur yield S_λ when melted; the allotropic distinction between these two forms, which is confined to the solid state, may thus be regarded as less fundamental than that between them and S_λ.

S_π is produced† by heating sulphur at 170° and then cooling rapidly. The solid product is dissolved in carbon disulphide, and the solution cooled to −80°; S_λ then crystallizes, leaving S_π in solution, and the latter is obtained, mixed with a little S_μ, when the solution is evaporated *in vacuo* at the same temperature.

* Vide *Chem. Soc. Ann. Reports*, 1918.
† Aten, *Proc. K. Akad. Wetensch. Amsterdam* (1918), **20**, 824.

S_μ, formed in quantity from S_λ at 250–300°, yields on solidification amorphous sulphur (plastic sulphur), insoluble in carbon disulphide, of which it is regarded as the liquid form.

Another crystalline form of sulphur,* known as S_ϕ, consisting of orange-yellow rhombohedra, which melt below 100°, and have a density of 2·135, is formed when hydrochloric acid at 0° is added to a cold solution of sodium thiosulphate, and the mixture is shaken with toluene.†

Regarding the molecular condition of sulphur in these allotropic forms, S_λ is believed to be S_8, S_ϕ and S_μ to be S_6, and S_π to be S_4. Sulphur vapour is S_8 near the boiling-point, but becomes S_2 at 1000°.

The three forms S_λ (S_α or S_β), S_π, and S_μ are distinguished by the colours they impart to solvents. Thus the solution of S_λ in carbon disulphide is nearly colourless, that of S_ϕ in toluene pale yellow, and that of S_π in the same solvent deep yellow like a concentrated solution of potassium chromate; whilst a solution of S_μ in pyridine is deep red. These colours are related to and may be the cause of those of the sulphides Na_2S, Na_2S_2, Na_2S_4, and Na_2S_5; indeed from Na_2S_5 solution acid precipitates S_μ, which forms the deep red solution in pyridine.

Amorphous sulphur.—Three forms of amorphous sulphur appear to exist: (i) an amorphous form, soluble in carbon disulphide, but insoluble in water, produced together with some of form (ii) when an aqueous solution of hydrogen sulphide is oxidized, or acid is added to a polysulphide. This may be the solid form of S_μ (precipitated sulphur, milk of sulphur).

(ii) A form insoluble in carbon disulphide and water, having a density of 1·955, and known as S_γ. This form is produced in small quantity, mixed with the form soluble in carbon disulphide, when a polysulphide solution is acidified. It is

* Engel, *compt. rend.* (1891), **112**, 866.
† Aten, *Zeitsch. phys. Chem.* (1914), **88**, 321.

present also in small amount in flowers of sulphur and plastic sulphur.

(iii) A colloidal form soluble in carbon disulphide and water, and known as S_δ, produced when hydrogen sulphide is passed through sulphurous acid solution at low temperature (Wackenroder's solution); and also when a saturated solution of sodium thiosulphate is decomposed by concentrated hydrochloric acid.

ALLOTROPIC FORMS OF SULPHUR

	Form.	Density.	M.P.	Molecule.	Solubility in CS₂.	Solubility in Water.
Crystalline.	$S\alpha$, rhombic ..	2·06	112·8	—	Sol.	Insol.
	$S\beta$, monoclinic, tabular, nacreous	1·96	119·25	—	Sol.	Insol.
	$S\pi$	—	—	S_4	—	—
	$S\phi$, rhombohedral	2·135	below 100°	S_6	—	—
Liquid	$S\lambda$	—	—	S_8	—	—
	$S\mu$	—	—	S_6	—	—
Amorphous.	?$S\mu$, precipitated S	—	—	?S_6	Sol.	Insol.
	$S\gamma$	1·955	—	—	Insol.	Insol.
	$S\delta$	—	—	—	Sol.	Sol.

Sulphur boils at 444·6° under 1 atm. pressure.

SELENIUM

Although not presenting the complexity of sulphur, selenium exists in various allotropic forms, which, according to Saunders, fall into three categories: (i) " liquid selenium ", including the amorphous, vitreous, and soluble or colloidal varieties; (ii) red, crystalline selenium, occurring in two different crystalline forms; (iii) metallic selenium.

(i) **Amorphous selenium** is formed as a red powder when cold selenious acid solution is reduced chemically, e.g. by sulphur dioxide, or electrolytically, and also when selenium is sublimed in a sealed tube. Its density is 4·26, and it is slightly soluble in carbon disulphide, benzene, and other solvents.

Vitreous selenium is obtained as a dark brown, brittle glass when fused selenium is rapidly cooled from above 217°. Its density is 4·28, and it is soluble in carbon disulphide.

Colloidal selenium is produced also by the reduction of selenious acid by sulphur dioxide or hydrazine, as well as by pouring a carbon disulphide solution of selenium into ether. It is a dark red powder which forms in water a red, fluorescent, colloidal solution from which amorphous selenium separates on standing or on the addition of an electrolyte.

(ii) **Red crystalline selenium** is formed when amorphous selenium stands in contact with carbon disulphide, or by the spontaneous evaporation of a carbon disulphide solution of selenium. There are two monoclinic varieties of density 4·47, which appear to melt at 170–180°, but quickly pass into the metallic form.

(iii) **Metallic selenium** is formed by melting selenium and keeping the liquid at 210° for some time. Thus transformation into the metallic form occurs, the mass crystallizes, and the temperature rises to 217°, the melting-point of the latter. Metallic selenium has a density of 4·80, and is insoluble in carbon disulphide; its electrical resistance decreases under the influence of light, a property employed for photometric purposes.

Selenium boils at 680°; its vapour density diminishes with rise of temperature, and at 950° corresponds to Se_2. Cryoscopic methods indicate Se_8 molecules.

Tellurium

Tellurium occurs in crystalline and amorphous forms.

Crystallized tellurium, obtained by fusion, consists of silvery white rhombohedra, having a density of 6·27 and melting at 452°.

Amorphous tellurium, obtained by reducing telluric acid solution by sulphurous acid or other reducing agent, has a density of 6·015, and when heated passes with heat evolution into the crystalline form. A colloidal form of tellurium is obtained by electrolytic reduction of a nitric-acid solution of the element.

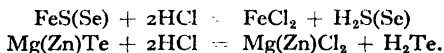
ALLOTROPIC FORMS OF SELENIUM AND TELLURIUM

Form.	Colour	Density.	Melting-point.	Solubility in CS_2.
Selenium				
Amorphous	Red	4·26	—	Soluble
Vitreous	Dark brown	4·28	—	,,
Colloidal	Red	—	—	,,
Crystalline (2 varieties), monoclinic	Red	4·47	170°–180°	,,
Metallic, hexagonal	Black	4·80	217°	Insoluble
Tellurium				
Crystalline, rhombohedra	Silvery white	6·27	452°	Insoluble
Amorphous	Greyish black	6·015	—	,,

HYDRIDES

The hydrides, XH_2, all result from the direct union of the elements, decrease of non-metallic character from oxygen to tellurium being exhibited by diminishing stability of the hydrides. Hydrogen and sulphur combine directly at about 400°, hydrogen and selenium at about 500°.

The oxides, sulphides, selenides, and tellurides of many metals (particularly those which give hydrogen with dilute acid), which have been produced by the direct union of the elements, yield hydrides by the action of acids; thus:

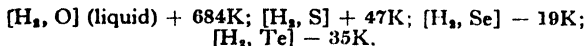
$$FeS(Se) + 2HCl = FeCl_2 + H_2S(Se)$$
$$Mg(Zn)Te + 2HCl = Mg(Zn)Cl_2 + H_2Te.$$

With the exception of water these compounds are all gases at ordinary temperature; they can, however, be liquefied and solidified with moderate ease, as the following figures show:

	H_2O	H_2S	H_2Se	H_2Te
Boiling-point at atm. press. ..	100°	−61·8°	−42°	−1·8°
Melting-point	0°	−85°	−64°	−57°

The boiling- and melting-points rise considerably in passing from sulphur to tellurium. The behaviour of water is seen to

be anomalous; and is probably accounted for, as previously suggested, by polymerization.

The variation of properties in a regular manner is shown in several ways. Thus, the heats of formation are:

$$[H_2, O] \text{ (liquid)} + 684K; \ [H_2, S] + 47K; \ [H_2, Se] - 19K; \ [H_2, Te] - 35K.$$

Parallel therewith, it is noticed that the ease of dissociation by heat increases with rise of molecular weight. Whilst water first dissociates at nearly 2000°, hydrogen sulphide is decomposed at 400–600°, and hydrogen selenide and telluride are resolved into their elements at lower temperatures (about 150°) than those at which they are produced by direct union, so that when the elements are heated below their boiling-points in hydrogen sublimation occurs.

Further, just as oxygen displaces sulphur from hydrogen sulphide, so sulphur displaces selenium from hydrogen selenide. And similarly, the reaction $H_2X + Cl_2 \rightarrow 2HCl + X$ occurs more readily with H_2S than with H_2O.

The hydrides of sulphur, selenium, and tellurium display feebly acidic properties, and react with solutions of metallic salts, yielding sulphides, selenides, and tellurides respectively. The position of water in this respect appears at first sight to be anomalous. Water behaves as a neutral oxide, and is described as *amphoteric*. As the first of the series of hydrides, it would be expected from analogy to be the most basic or least acidic, and such is actually the case. In a comparison of the properties of the hydrides of the fifth group, it was found that whilst ammonia is basic, and phosphine practically neutral, acidic properties begin to appear with the hydrides of arsenic and antimony, inasmuch as an unstable arsenide and a more stable antimonide are formed when these gases react with silver-nitrate solution. Now in chemical properties water bears approximately the same relation to phosphine as sulphuretted hydrogen does to arsine; in each case there is a slight diminution of basic properties in passing from the fifth to the sixth group It was further observed that the basic

properties of the hydrides of the fifth group are increased by substitution of alkyl groups for hydrogen. The same fact is observable in the sixth group, since methyl oxide combines with hydrogen chloride to form dimethyloxonium chloride, $O(CH_3)_2HCl$, previously mentioned, a derivative of the hypothetical oxonium radicle $(OH_3)^+$; derivatives of hydrogen sulphide give rise to the sulphonium compounds, SR_3X, whilst selenonium compounds are similarly derived from hydrogen selenide.* It will appear from these considerations that the neutral properties of water are to be expected from the periodic law; and even the condensibility of this compound, and the existence of complex molecules in the liquid state, find a parallel in the case of hydrogen fluoride in the seventh group.

Hydrogen persulphides are present in the oil which separates when a solution of alkali polysulphide is poured into concentrated hydrochloric acid at low temperature. H_2S_2, H_2S_3, and H_2S_5 have been isolated, and H_2S_6 is believed to exist.

Halides

These are of several types:

	F′	Cl′	Br′	I′
X_2R_2	S_2F_2	S_2Cl_2	S_2Br_2	—
		Se_2Cl_2	Se_2Br_2	-
XR_2	—	SCl_2	—	—
		$TeCl_2$	$TeBr_2$	—
XR_4	SF_4	SCl_4	—	-
	SeF_4	$SeCl_4$	$SeBr_4$	—
	TeF_4	$TeCl_4$	$TeBr_4$	TeI_4
XR_6	SF_6	—	—	—
	SeF_6	—	—	—
	TeF_6	—	—	—
Other types	S_2F_{10}	S_3Cl_4	—	—

The inclusion of the oxygen compounds of the halogens among the halides of Group VI is not warranted, for whilst the typical halides of this group are halanhydrides corresponding with certain oxyacids, the oxygen compounds Cl_2O, ClO_2,

* See also Iodonium compounds, p. 445.

and I_2O_5 are anhydrides of the halogen oxyacids, and are therefore dealt with under Group VII.

The Group VI halides result in general from direct union of the elements, the type of halide produced depending on the relative proportions of the reacting substances and the conditions of the experiment. **Sulphur monochloride,** for instance, is stable, and can be distilled; the dichloride exists and gives double compounds, e.g. $AsCl_3 \cdot SCl_2$. By the further action of chlorine on the monochloride at $-22°$ the unstable **tetrachloride** results, SCl_4 or $[SCl_3]Cl$ (Lowry, 1929). **Sulphur hexafluoride,** SF_6, formed by the combination of its elements, is a colourless stable gas. It is noteworthy that SF_2 is unknown and SF_4 doubtful; thus the tendency of fluorine to form polyfluorides is again emphasized. SeF_4 has, however, been obtained.* **Selenium** first yields a **monochloride,** Se_2Cl_2, by the action of chlorine; it gives no dichloride, but its **tetrachloride** can be distilled. **Tellurium** forms the **dichloride** and stable **tetrachloride**, and the only definite iodide, TeI_4, the type M_2X_2 not being represented by the halides of this element.

The type XR_4 represents the halanhydrides of the ortho-acids $X(OH)_4$, corresponding with the dioxides; these, however, do not exist, and the halides of this type when decomposed by water yield the $OX(OH)_2$ acids, derived from the $X(OH)_4$ type by dehydration; for instance,

$$TeCl_4 + 3H_2O = H_2TeO_3 + 4HCl.$$

The tetrachlorides of selenium and tellurium, however, first yield the oxychlorides, $SeOCl_2$ and $TeOCl_2$, which are finally decomposed, giving the oxyacids.

There are no oxyacids corresponding with any type of halide lower than XR_4. The lower halides are, however, decomposed by water, with the formation of oxyacids of the type $OX(OH)_2$ and separation of the elements; for example,

$$2S_2Cl_2 + 3H_2O = 3S + H_2SO_3 + 4HCl.$$

* Prideaux and Cox, *J. Chem. Soc.* (1927), 928.

THE OXIDES

Oxides of a number of types are known:

XO	SO	SeO(?)	TeO
X_2O_3	S_2O_3	($SeSO_3$ $TeSO_3$,	$TeSeO_3$)
XO_2	SO_2	SeO_2	TeO_2
XO_3	SO_3	SeO_3	TeO_3
X_2O_7	S_2O_7	—	—
XO_4	SO_4	—	—

Of these the type XO is unimportant, the existence of SeO being doubtful, and TeO giving rise to no salts. The acidic oxides XO_2 and XO_3, in the latter of which the maximum oxygen valency is displayed, are the most characteristic, and correspond with the oxyacids $OX(OH)_2$ and $O_2X(OH)_2$, the more completely hydroxylated types $X(OH)_4$, $OX(OH)_4$, and $X(OH)_6$ being known only in $Te(OH)_6$ and certain basic sulphates, e.g. $OS(O_2Pb)_2$ and $S(O_2Hg^{\cdot\cdot})_3$. Tellurium dioxide has also feebly basic properties, yielding unstable salts such as $Te(SO_4)_2$; this is in harmony with the position of tellurium in the group.

Oxides of the type X_2O_3 will be dealt with later.

OXIDES XO_2 AND DERIVED ACIDS

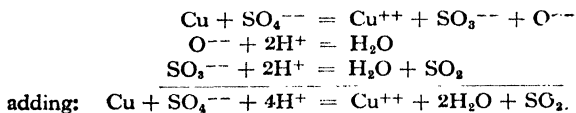
The oxides XO_2, known for each element, result from the direct union of the elements with oxygen. While **sulphur dioxide** is a gas easily condensible to a liquid, boiling at —8°, **selenium dioxide** is a crystalline solid subliming at about 300°, and **tellurium dioxide** also a solid easily melting to a yellowish liquid, which boils without decomposition.

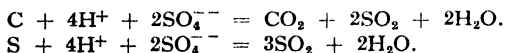
It will be remembered in the case of the fifth group that phosphorus forms phosphoric oxide, and arsenic arsenious oxide, on combustion. The analogous elements of the sixth group unite spontaneously with a less atomic proportion of oxygen than phosphorus, being rather analogous to arsenic in power of oxidation; and those of the seventh group are non-combustible, though, indeed, all form oxides. Sulphur approximates to phosphorus in forming a little of the higher

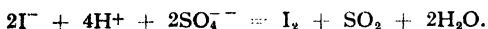
oxide by direct combustion. When selenium and tellurium are warmed with nitric acid they yield selenious and tellurious acids, H_2SeO_3 and H_2TeO_3, respectively, each of which exists in the solid state. Associated with this physical property of the acids is that of easy dehydration, for these two acids readily yield their anhydrides; TeO_2, indeed, separates from the nitric-acid solution of the element.

This tendency towards dehydration is manifested by acids derived from metalloids or weak metals, whose oxides are feeble anhydrides. Sometimes poly-acids or their salts exist, representing intermediate products of dehydration, as in the case of chromic, molybdic, and tungstic acids. Oxides of non-metals which are powerful anhydrides, e.g. N_2O_5, P_2O_5, SO_3, combine with, and retain, water with avidity, and the acids are generally liquids or solids of low melting-point.

The dioxides, XO_2, may also be obtained by reduction of the XO_3 oxides or the corresponding H_2XO_4 acids; as, for example, in the well-known method of preparation of sulphur dioxide from sulphuric acid by warming the concentrated acid with metals (such as Cu, Ag, Hg, Zn), or with carbon or sulphur. In these reactions the sulphate ion may be regarded as acting as an oxidizing agent; thus:

$$\begin{aligned} Cu + SO_4^{--} &= Cu^{++} + SO_3^{--} + O^{--} \\ O^{--} + 2H^+ &= H_2O \\ SO_3^{--} + 2H^+ &= H_2O + SO_2 \\ \text{adding:}\quad Cu + SO_4^{--} + 4H^+ &= Cu^{++} + 2H_2O + SO_2. \end{aligned}$$

Here copper is oxidized from the metallic to the cupric state. Secondary reactions occur by which CuS and finally Cu_2S are formed (*vide* p. 143).

$$\begin{aligned} C + 4H^+ + 2SO_4^{--} &= CO_2 + 2SO_2 + 2H_2O. \\ S + 4H^+ + 2SO_4^{--} &= 3SO_2 + 2H_2O. \end{aligned}$$

Similarly, concentrated sulphuric acid oxidizes hydriodic acid, and less readily also hydrobromic acid:

$$2I^- + 4H^+ + 2SO_4^{--} = I_2 + SO_2 + 2H_2O.$$

Loss of oxygen may occur even by simple heating; thus SO_3 and TeO_3 are both decomposed into the dioxides and oxygen when heated strongly, whilst SeO_3 is similarly decomposed when heated to 120°.

The acids, H_2XO_3, corresponding with the XO_2 oxides, represent the first and only meta-derivatives of the hypothetical type, $X(OH)_4$; they are **sulphurous, selenious,** and **tellurious acids.** Sulphur and selenium dioxides both dissolve in water, yielding the acids, but tellurium dioxide is only very slightly soluble in water and alkalis, and its aqueous solution does not redden blue litmus. Whilst selenious and tellurious acids can both be isolated in the pure state, sulphurous acid belongs to the category of easily decomposable acids (such as carbonic, silicic, nitrous), readily giving sulphur dioxide when the aqueous solution is heated, although solid crystallohydrates separate from saturated aqueous solutions at low temperatures. The instability of sulphurous acid may be attributed partly to the gaseous nature of sulphur dioxide, but is also due to its feebly anhydride character.

It is remarkable that while sulphurous acid acts as a reducing agent, selenious acid is itself easily reduced, for example by sulphur dioxide or organic matter. Sulphurous acid is, however, reduced by a powerful reducing agent such as phosphorous acid, sulphur being precipitated. The affinity of selenium for oxygen appears to be less than the affinities of its allied elements, as is further shown by the readiness with which SeO_3 decomposes into the dioxide and oxygen.

These acids are dibasic, giving rise to normal salts, such as in the case of sulphur, Na_2SO_3, K_2SO_3, $CaSO_3$, and to acid salts, such as the hydrogen sulphites, $NaHSO_3$ and $KHSO_3$, and the pyro- or disulphites $Na_2S_2O_5$ and $K_2S_2O_5$.

Pyroselenites and pyrotellurites analogous to pyrosulphites are unknown.

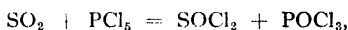
The hydrogen sulphites are precipitated by alcohol from cold sulphite solutions which have been saturated with sulphur dioxide; the pyrosulphites are obtained by evaporating the

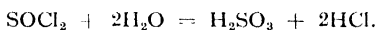
hydrogen-sulphite solutions, or in the case of the sodium salt by the interaction of solid Na_2CO_3, H_2O and sulphur dioxide gas.

The oxychloride, $SOCl_2$, thionyl chloride, a colourless liquid boiling at 78°, which may be obtained by the action of phosphorus pentachloride on sodium sulphite,

$$Na_2SO_3 + 2PCl_5 = 2NaCl + SOCl_2 + 2POCl_3,$$

or by the reaction

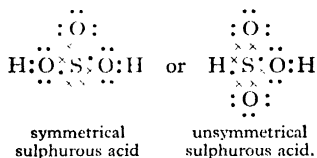
$$SO_2 + PCl_5 = SOCl_2 + POCl_3,$$

corresponds with H_2SO_3, into which it is converted by water, and of which, therefore, it is the chloride:

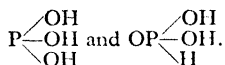
$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl.$$

With alcohol it yields, similarly, the ethyl ester $(C_2H_5)_2SO_3$.

Constitution of H_2XO_3 Acids

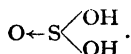
In considering the structure of sulphurous acid and its salts two possibilities are presented; the acid may be formulated:

```
        ..                 ..
       :O:                :O:
  ..    x   ..             xx  ..
H:O:S:O:H      or    H:S:O:H
  ..   xx   ..             xx  ..
                          :O:
                           ..
```

symmetrical sulphurous acid — unsymmetrical sulphurous acid.

the metallic salts possessing corresponding constitutions; just as with phosphorous acid there are the two possible structures:

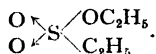
```
  /OH          /OH
P—OH  and  OP—OH.
  \OH          \H
```

It may be pointed out that such dual structures of hydroxy-compounds are theoretically possible in all cases where the nuclear atom is incompletely oxidized; and it is to be supposed that the stability of the unsymmetrical form will depend on the oxidizability of this atom.

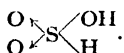
Now the structure of thionyl chloride must almost certainly be $O \leftarrow S \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$, and that of the ethyl salt, formed by interaction of thionyl chloride and alcohol, is therefore $O \leftarrow S \begin{matrix} \diagup OC_2H_5 \\ \diagdown OC_2H_5 \end{matrix}$; thus it is symmetrical ethyl sulphite, and is a liquid boiling at 161°. Similarly, aqueous sulphurous acid, which may be obtained by causing thionyl chloride to react with water, must possess, at least at the moment of its formation, the formula

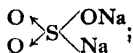
$$O \leftarrow S \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}.$$

Ethyl sulphite, when treated with sodium hydroxide, is hydrolyzed, yielding sodium sulphite and alcohol; and when sodium sulphite is digested with ethyl iodide, a product is obtained according to the reaction

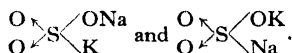
$$Na_2SO_3 + 2C_2H_5I = (C_2H_5)_2SO_3 + 2NaI,$$

which, however, is not identical with the ethyl sulphite described above, since it boils at 213°. Moreover, when hydrolyzed, this product yields sodium ethylsulphonate, $NaC_2H_5SO_3$, a salt of ethylsulphonic acid. And since ethylsulphonic acid results from the oxidation of mercaptan, C_2H_5SH, in which ethyl is undoubtedly attached to sulphur, it follows that the above isomer, boiling at 213°, is ethyl ethylsulphonate:

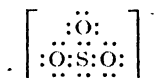
$$\begin{matrix} O \nwarrow \\ O \swarrow \end{matrix} S \begin{matrix} \diagup OC_2H_5 \\ \diagdown C_2H_5 \end{matrix}.$$

and is derived from unsymmetrical sulphurous acid:

$$\begin{matrix} O \nwarrow \\ O \swarrow \end{matrix} S \begin{matrix} \diagup OH \\ \diagdown H \end{matrix}.$$

Sodium sulphite, which gives rise to this derivative, might therefore be represented thus:

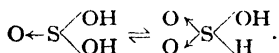
$$\begin{matrix} O \nwarrow \\ O \swarrow \end{matrix} S \begin{matrix} \diagup ONa \\ \diagdown Na \end{matrix};$$

and this unsymmetrical formula suggests the existence of two isomeric sodium potassium sulphites,

$$\begin{matrix} O \nwarrow \\ O \swarrow \end{matrix} S \begin{matrix} \diagup ONa \\ \diagdown K \end{matrix} \quad \text{and} \quad \begin{matrix} O \nwarrow \\ O \swarrow \end{matrix} S \begin{matrix} \diagup OK \\ \diagdown Na \end{matrix} .$$

These, however, have not been prepared, and, according to modern views of molecular structure, should not exist.

For it is now generally believed that salts are ionized in their formation, and exist in the solid state as ions held together by electrostatic attraction. Thus the SO_3'' ion is always the same;

$$\left[\begin{matrix} :\ddot{O}: \\ :\ddot{O}:\ddot{S}:\ddot{O}: \end{matrix} \right]^{..}$$

and it is only when radicles such as C_2H_5 are attached in different ways to SO_3 to form non-ionized molecules that isomerism can occur.

These considerations, however, leave the constitution of non-ionized sulphurous acid itself unsettled; so that the acid may be an equilibrium mixture,

$$O \leftarrow S \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} \rightleftharpoons \begin{matrix} O \nwarrow \\ O \swarrow \end{matrix} S \begin{matrix} \diagup OH \\ \diagdown H \end{matrix} .$$

This state disappears in the course of salt formation.

Selenious and tellurious acids do not present phenomena analogous to those described above in the case of sulphurous acid.

Ethyl selenite, $O \leftarrow Se \begin{matrix} \diagup OC_2H_5 \\ \diagdown OC_2H_5 \end{matrix}$, is obtained both by the action of sodium ethoxide on selenosyl chloride, $O \leftarrow Se \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$, and of ethyl iodide on silver selenite. Selenious acid appears, therefore, to yield symmetrical derivatives even from its inorganic salts, and the same is probably true of tellurious acid; this difference may be attributed to the inferior oxidizability of selenium and tellurium as compared with sulphur.

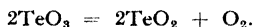
Oxides XO_3 and Derived Acids

Sulphur trioxide, SO_3, is formed by the union of sulphur dioxide with ozone, or with oxygen in presence of a catalyst. Platinized asbestos is the catalyst usually employed, but oxides of iron (burnt pyrites), copper, chromium, and vanadium have been employed. The optimum temperature for the reaction with a platinum catalyst is 400–450° C.; and with a gaseous mixture of 7 per cent of SO_2, 10·4 per cent of oxygen, and 82·6 per cent of nitrogen, obtained by burning pyrites in air, more than 90 per cent of the SO_2 can be converted into SO_3. It has been found that the platinum is " poisoned ", so as to become inactive, by impurities in the gases, especially by arsenious oxide and dust, which must be carefully removed. The sulphur trioxide so produced cannot be absorbed in water, with which it produces an uncondensible fog of sulphuric acid droplets. On the large scale, therefore, it is absorbed in the concentrated acid forming fuming sulphuric acid, or oleum.

Sulphur trioxide exists in two forms; α-SO_3 is a liquid boiling at 46°, and forming crystals which melt at 14·8°; on standing, this form passes into β-SO_3, consisting of silky needles, which at 50° revert to the α-form. The α-form consists of SO_3 molecules, the β-form of S_2O_6 molecules. According to Smits (1926), there are three forms; the α-SO_3 above, and two others melting at 62·2° and 32·5°, respectively. Sulphur trioxide fumes in moist air.

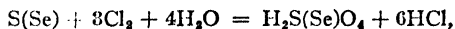
Selenium trioxide, SeO_3, is said to be formed, mixed with SeO_2, when dry oxygen reacts with selenium under the influence of a high frequency discharge (Rheinboldt, 1930). It is a white hygroscopic powder.

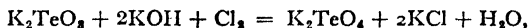
Tellerium trioxide, TeO_3, formed as a dark-yellow powder by heating telluric acid, decomposes thus when heated:

$$2TeO_3 = 2TeO_2 + O_2.$$

The acids H_2XO_4 are represented by sulphuric, selenic, and telluric acids. Of the anhydrides, SO_3 and TeO_3, SO_3 alone unites directly with water, TeO_3 being unaltered by it (cf. TeO_2).

Each of the acids of this type is produced by the oxidation either of the element or of the lower acid; as, for instance, in the case of sulphurous acid by the catalytic action of the lower oxides of nitrogen in the sulphuric-acid chamber process.

Sulphur and selenium are oxidized by chlorine in the presence of water, thus:

$$S(Se) + 3Cl_2 + 4H_2O = H_2S(Se)O_4 + 6HCl,$$

and potassium tellurate results from the action of chlorine on the tellurite in alkaline solution,

$$K_2TeO_3 + 2KOH + Cl_2 = K_2TeO_4 + 2KCl + H_2O,$$

free telluric acid being obtained from the potassium salt by conversion, by means of barium chloride, into the sparingly soluble barium tellurate, which is then decomposed by the requisite amount of sulphuric acid. Each of these acids may be obtained in the pure state.

Sulphuric acid melts at 10·5°; **selenic acid** at 58°; **telluric acid** does not melt.

Sulphuric and selenic acids readily unite with water, forming crystallohydrates; telluric acid forms the crystalline compound, H_2TeO_4, $2H_2O$, which appears to be a hexabasic acid, H_6TeO_6, since it forms not only salts of this type, but also the ester $Te(OCH_3)_6$.

The three acids differ in important respects, and their differences serve further to illustrate the periodic variation of properties. Thus sulphuric acid of 98·3 per cent H_2SO_4 distils at 330°, and only breaks up into sulphur dioxide, water, and oxygen at a red heat; but selenic acid begins to decompose into selenium dioxide, oxygen, and water at about 280°, and telluric acid at a low red heat easily gives the anhydride, and then the dioxide and oxygen.

Owing to the greater ease with which they lose oxygen, selenic and telluric acids are more powerful oxidizing agents than sulphuric acid. For example, sulphuric acid does not act upon hydrochloric acid, but selenic and telluric acids both

yield, with strong hydrochloric acid, the lower acids and chlorine; thus:

$$H_2Se(Te)O_4 + 2HCl = H_2Se(Te)O_3 + Cl_2 + H_2O.$$

Thus $BaSeO_4$ differs from $BaSO_4$ by dissolving in strong hydrochloric acid. As dibasic acids, each of these acids gives rise to both normal and acid salts of the types $M^{\cdot}_2XO_4$ and $M^{\cdot}HXO_4$. On careful heating, the acid or hydrogen sulphates of the alkali metals produce pyrosulphates by loss of water; e.g.:

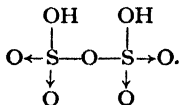
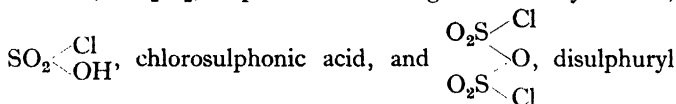
$$2KHSO_4 = K_2S_2O_7 + H_2O.$$

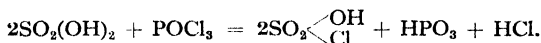
Telluric acid further forms acid salts, such as K_2TeO_4, TeO_3, $4H_2O$, and K_2TeO_4, $3TeO_3$, $4H_2O$, a behaviour recalling that of chromic acid in producing the di- and trichromates. Tellurium shows a further resemblance to the members of Group VI A by forming complex phospho- and arsenitelluric acids.

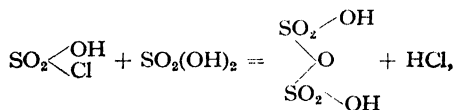
Selenates are isomorphous with sulphates, and form alums, but tellurates are more closely allied to chromates, with which they are sometimes isomorphous.

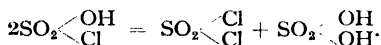
Without doubt, selenates resemble sulphates in structure, both acids being of comparable strength. Telluric acid, however, is a very weak acid, and most probably is H_6TeO_6, from which by careful dehydration allotelluric acid, possibly $(H_2TeO_4)_n$ may be obtained. Both forms may exist in solution. No isomerism analogous to that of ethyl sulphite and ethyl ethylsulphonate is known, so that in the alkyl sulphates there is no reason to suppose that either of the alkyl groups is not attached to oxygen.

Pyro- or disulphuric acid, which separates from oleum, Nordhausen, or fuming sulphuric acid in crystals melting at 35°, is formulated thus:

```
      OH    OH
      |     |
  O←S—O—S→O.
      ↓     ↓
      O     O
```

Each of the above acids further corresponds with an oxy-chloride, XO_2Cl_2, sulphur also forming the half-oxychloride, $SO_2\!<\!\begin{smallmatrix}Cl\\OH\end{smallmatrix}$, chlorosulphonic acid, and $\begin{smallmatrix}O_2S\!-\!Cl\\ \quad >O\\ O_2S\!-\!Cl\end{smallmatrix}$, disulphuryl chloride, corresponding with disulphuric acid.

Chlorosulphonic acid is prepared by the direct union of sulphuric anhydride and dry hydrogen chloride, or by the action of phosphorus oxychloride on sulphuric acid,

$$2SO_2(OH)_2 + POCl_3 = 2SO_2\!<\!\begin{smallmatrix}OH\\Cl\end{smallmatrix} + HPO_3 + HCl.$$

It is a colourless liquid boiling at 152°, and easily decomposed by water, giving sulphuric and hydrochloric acids; with strong sulphuric acid, disulphuric and hydrochloric acids are formed,

$$SO_2\!<\!\begin{smallmatrix}OH\\Cl\end{smallmatrix} + SO_2(OH)_2 = \begin{smallmatrix}SO_2\!-\!OH\\ \quad >O\\ SO_2\!-\!OH\end{smallmatrix} + HCl,$$

and when heated alone at 180° it is resolved into sulphuryl chloride and sulphuric acid,

$$2SO_2\!<\!\begin{smallmatrix}OH\\Cl\end{smallmatrix} = SO_2\!<\!\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + SO_2\!<\!\begin{smallmatrix}OH\\OH\end{smallmatrix}.$$

Sulphuryl chloride, SO_2Cl_2, is also prepared, however, by the direct union of sulphur dioxide and chlorine, a reaction which occurs slowly in strong light, but which is readily brought about by allowing the gases to come into contact with camphor, the rôle of this substance in the reaction being unknown. It is a colourless liquid boiling at 69°, and like chlorosulphonic acid is converted by water into sulphuric and hydrochloric acids; it is thus the true chloride of sulphuric acid.

OTHER OXYACIDS OF SULPHUR

In addition to the characteristic types of sulphurous and sulphuric, sulphur gives rise to a considerable number of other oxyacids, which are here enumerated:

Sulphoxylic acid, H_2SO_2,
Hyposulphurous acid, $H_2S_2O_4$,
Thiosulphuric acid, $H_2S_2O_3$,
Dithionic (hyposulphuric) acid, $H_2S_2O_6$,
Trithionic acid, $H_2S_3O_6$,
Tetrathionic acid, $H_2S_4O_6$,
Pentathionic acid, $H_2S_5O_6$,
[Hexathionic acid, $H_2S_6O_6$].*

Corresponding with thiosulphuric acid there is also selenosulphuric acid, H_2SeSO_3, and with trithionic acid, selenotrithionic acid, $H_2SeS_2O_6$.

Persulphuric acid (perdisulphuric acid), $H_2S_2O_8$, and permonosulphuric acid or " Caro's acid ", H_2SO_5, along with the anhydride S_2O_7, belong to the class of " per " compounds, and will be dealt with in a separate section.

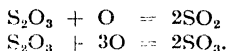
Hyposulphurous acid.—The zinc salt of this acid is produced when sulphurous-acid solution is treated with zinc, the metal dissolving without evolution of hydrogen. When sodium-hydrogen-sulphite solution is used, sodium hyposulphite† results, and may be obtained crystalline, $Na_2S_2O_4$, $2H_2O$. Free hyposulphurous acid has never been obtained in the pure state. The hyposulphites are powerful reducing agents, bleaching organic matter and precipitating silver and mercury and cuprous hydride from the corresponding salt solutions. On account of the former action they receive commercial application. They readily absorb oxygen, yielding sulphites and sulphates.

The formula H_2SO_2 was attributed to hyposulphurous acid by the discoverer, Schützenberger. This would correspond with an anhydride, SO, whilst $H_2S_2O_4$ corresponds with S_2O_3. The formula $H_2S_2O_4$ was proved by Bernthsen thus: Ammoniacal copper sulphate oxidizes hyposulphite to sul-

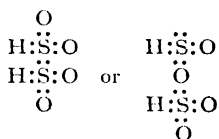
* Potassium hexathionate exists, vide Partington and Tipler, *J. Chem. Soc.* (1929), 1382.

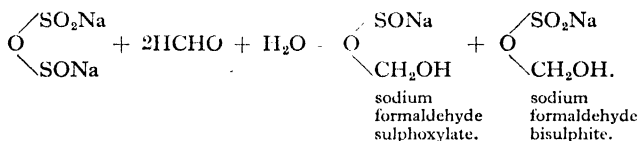
† Sometimes called hydrosulphite.

phite, iodine oxidizes it to sulphate. It was found that for every two atoms of sulphur as hyposulphite, one atom of oxygen is required to oxidize to sulphite, and three to sulphate; thus:

$$S_2O_3 + O = 2SO_2$$
$$S_2O_3 + 3O = 2SO_3.$$

Therefore hyposulphite corresponds with the anhydride S_2O_3 rather than with SO.

The constitution of hyposulphurous acid may be expressed thus, only necessary electrons being shown:

$$\begin{array}{c} \mathrm{O} \\ \mathrm{H}:\ddot{\mathrm{S}}:\mathrm{O} \\ \mathrm{H}:\ddot{\mathrm{S}}:\mathrm{O} \\ \ddot{\mathrm{O}} \end{array} \quad \text{or} \quad \begin{array}{c} \mathrm{H}:\ddot{\mathrm{S}}:\mathrm{O} \\ \ddot{\mathrm{O}} \\ \mathrm{H}:\ddot{\mathrm{S}}:\mathrm{O} \\ \ddot{\mathrm{O}} \end{array}$$

Since dithionic acid, in which two sulphur atoms are joined together, is not formed by its oxidation, the second formula is preferable, and represents it as a mixed anhydride of sulphoxylic and sulphurous acids. This accords with the reaction of formaldehyde on the sodium salt:

$$O\begin{array}{l} \diagup SO_2Na \\ \diagdown SONa \end{array} + 2HCHO + H_2O = \underset{\substack{\text{sodium}\\\text{formaldehyde}\\\text{sulphoxylate.}}}{O\begin{array}{l} \diagup SONa \\ \diagdown CH_2OH \end{array}} + \underset{\substack{\text{sodium}\\\text{formaldehyde}\\\text{bisulphite.}}}{O\begin{array}{l} \diagup SO_2Na \\ \diagdown CH_2OH. \end{array}}$$

Sodium formaldehyde-sulphoxylate (M.P. 63°) is stable at ordinary temperature, but exhibits strong reducing properties at steam heat.

Sulphoxylic acid, H_2SO_2, is not known free, but the zinc salt is formed when zinc dust acts on sulphuryl chloride in ether solution.

$$SO_2Cl_2 + 2Zn = ZnCl_2 + ZnSO_2.$$

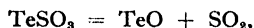
The soluble stable sodium salt is known.

Sulphur monoxide, SO, is prepared by the action of an electric discharge on a mixture of sulphur dioxide and sulphur

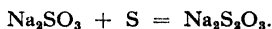
vapour at low pressure. It is also formed when sulphur burns at low pressure, and when thionyl chloride, $SOCl_2$, is heated with silver or magnesium.

It is a gas at room temperature, stable to dry oxygen, but reacts with water and alkali to give sulphide, sulphite, and sulphur (P. W. Schenk, 1935). No polythionates are formed, contrary to the assumption that it was an intermediate compound in the reaction between H_2S and SO_2 in Wackenroder's solution (q.v.). It reacts with metals to form sulphides, and decomposes at high temperature to give sulphur dioxide and sulphur.

Sulphur sesquioxide, S_2O_3, is obtained as a blue-green crystalline mass by the direct union of sulphur and sulphur trioxide. The beautiful indigo-blue colour formed when Nordhausen acid is poured on flowers of sulphur is due to this oxide. The sesquioxide does not give hyposulphurous acid with water, but decomposes,* producing sulphur, trithionic and pentathionic acids, $H_2S_3O_6$ and $H_2S_5O_6$, respectively. Sulphoxylic acid, H_2SO_2, is also probably present. On the analogy of the thermal decomposition of tellurium sulphoxide, $TeSO_3$, whereby TeO is formed:

$$TeSO_3 = TeO + SO_2,$$

it might be expected that S_2O_3 would in similar fashion yield SO. Schenk (1933) found no evidence of SO, but obtained an orange solid, probably S_2O_2.

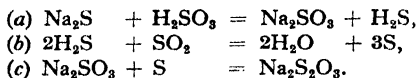
Thiosulphuric acid, $H_2S_2O_3$, still commonly called hyposulphurous acid, is not known in the pure state, although dilute solutions are formed by the action of flowers of sulphur on sulphurous acid at about 80°. The salts, however, are more stable. They are produced by the action of sulphur on the sulphites, thus:

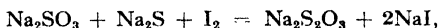
$$Na_2SO_3 + S = Na_2S_2O_3.$$

Selenium similarly dissolves in Na_2SO_3, forming Na_2SeSO_3.

The formation of thiosulphate on a large scale, by leading

* Vogel and Partington, *J. Chem. Soc. Trans.* (1925), **127**, 1521.

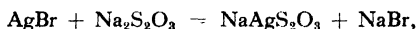
sulphur dioxide into alkali or alkaline-earth sulphide solutions, depends on the same reaction, as the following equations show:

$$(a)\ Na_2S + H_2SO_3 = Na_2SO_3 + H_2S,$$
$$(b)\ 2H_2S + SO_2 = 2H_2O + 3S,$$
$$(c)\ Na_2SO_3 + S = Na_2S_2O_3.$$

When iodine acts on a mixture of alkali sulphite and sulphide, a thiosulphate results:

$$Na_2SO_3 + Na_2S + I_2 = Na_2S_2O_3 + 2NaI,$$

and sodium thiosulphate is reduced by sodium amalgam, so that sulphite and sulphide are reproduced,

$$Na_2S_2O_3 + 2Na = Na_2SO_3 + Na_2S.$$

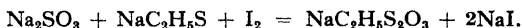
Sodium thiosulphate, $Na_2S_2O_3,5H_2O$, is used for "fixing" photographic negatives and prints on account of the reaction:

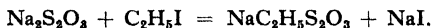
$$AgBr + Na_2S_2O_3 = NaAgS_2O_3 + NaBr,$$

and as an "antichlor" in bleaching because it reacts with chlorine or hypochlorite thus:

$$Na_2S_2O_3 + 4HOCl + H_2O = Na_2SO_4 + H_2SO_4 + 4HCl.$$

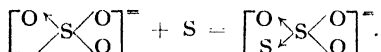
It is noteworthy that the reaction of thiosulphate with iodine differs entirely from that with chlorine in presence of water; this is probably due to the fact that the latter reaction is really one of oxidation by hypochlorous acid, as the equation shows.

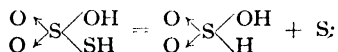
If sodium ethyl sulphide is substituted for sodium sulphide in the above reaction with iodine, sodium ethyl thiosulphate (Bunte's salt) results, thus:

$$Na_2SO_3 + NaC_2H_5S + I_2 = NaC_2H_5S_2O_3 + 2NaI.$$

The same salt is formed when ethyl iodide reacts with sodium thiosulphate:

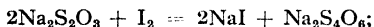
$$Na_2S_2O_3 + C_2H_5I = NaC_2H_5S_2O_3 + NaI.$$

There is no doubt that the thiosulphates must be considered as sulphates in which one atom of oxygen has been replaced

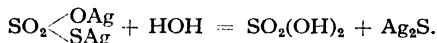
by one atom of sulphur, the addition of sulphur to a sulphite ion resembling the addition of oxygen,

$$\left[\begin{matrix}O\nwarrow \\ \diagup\end{matrix}S\begin{matrix}\diagup O \\ \diagdown O\end{matrix}\right]^{=} + S = \left[\begin{matrix}O\nwarrow \\ S\swarrow\end{matrix}S\begin{matrix}\diagup O \\ \diagdown O\end{matrix}\right]^{=}.$$

Thiosulphuric acid readily parts with sulphur, forming sulphurous acid, as is shown by the separation of this element from an acidified solution of a thiosulphate thus:

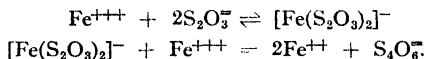
$$\begin{matrix}O\nwarrow \\ O\swarrow\end{matrix}S\begin{matrix}\diagup OH \\ \diagdown SH\end{matrix} = \begin{matrix}O\nwarrow \\ O\swarrow\end{matrix}S\begin{matrix}\diagup OH \\ \diagdown H\end{matrix} + S;$$

and the relationship of the acid to sulphuric acid is illustrated by the hydrolysis by water of such salts as the thiosulphates of silver and cobalt according to reaction (ii) below.

Two characteristic reactions of thiosulphate are: (i) condensation to tetrathionate, as with iodine thus:

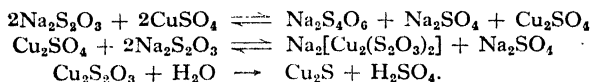
$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6;$$

and (ii) hydrolysis to sulphide and sulphuric acid, as with silver thiosulphate, thus:

$$SO_2\begin{matrix}\diagup OAg \\ \diagdown SAg\end{matrix} + HOH = SO_2(OH)_2 + Ag_2S.$$

In the light of these reactions the behaviour of ferric chloride and of copper sulphate with sodium thiosulphate is interesting.

Thus when ferric chloride solution is added drop by drop to sodium thiosulphate there is first a purple colour, due to a complex ferric thiosulphate, and then the solution becomes colourless as the ferric iron is reduced to the ferrous condition, and the thiosulphate is oxidized to tetrathionate, thus:

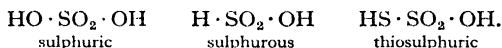
$$Fe^{+++} + 2S_2O_3^{=} \rightleftharpoons [Fe(S_2O_3)_2]^{-}$$
$$[Fe(S_2O_3)_2]^{-} + Fe^{+++} = 2Fe^{++} + S_4O_6^{=}.$$

The condensation to tetrathionate by means of iodine is effected by the oxidizing action of the iodine atoms, which are reduced to iodide ions. With chlorine, which produces hypochlorous acid, thiosulphate is oxidized to sulphate and sulphuric acid. When copper sulphate solution is added

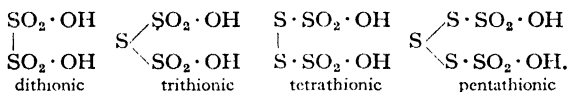
drop by drop to sodium thiosulphate there is first a discharge of the blue colour owing to reduction to the cuprous state, followed by a precipitation of cuprous sulphide when the solution is boiled. The following reactions occur:

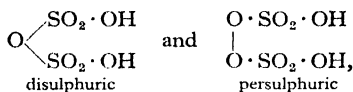
$$2Na_2S_2O_3 + 2CuSO_4 \rightleftharpoons Na_2S_4O_6 + Na_2SO_4 + Cu_2SO_4$$
$$Cu_2SO_4 + 2Na_2S_2O_3 \rightleftharpoons Na_2[Cu_2(S_2O_3)_2] + Na_2SO_4$$
$$Cu_2S_2O_3 + H_2O \rightarrow Cu_2S + H_2SO_4.$$

Thus the reactions with copper sulphate combine those of condensation and hydrolysis of thiosulphate.

Thionic Acids

Both sulphurous and thiosulphuric acids contain the group $SO_2 \cdot OH$, which is characteristic of sulphonic acids, such as benzene sulphonic acid, $C_6H_5 \cdot SO_2 \cdot OH$. The relationship to sulphuric acid is made clear by the formulæ:

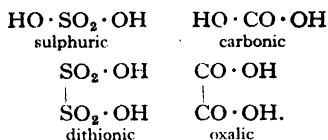
$HO \cdot SO_2 \cdot OH$	$H \cdot SO_2 \cdot OH$	$HS \cdot SO_2 \cdot OH$.
sulphuric	sulphurous	thiosulphuric

Similarly, the thionic acids may be regarded as sulphonic acids obtained either by direct union of sulphonic groups or their linkage through a sulphur atom or atoms. Their structures are indicated by the following formulæ:

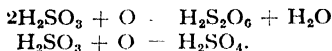
$SO_2 \cdot OH$ | $SO_2 \cdot OH$	$S \langle {SO_2 \cdot OH \atop SO_2 \cdot OH}$	$S \cdot SO_2 \cdot OH$ | $S \cdot SO_2 \cdot OH$	$S \langle {S \cdot SO_2 \cdot OH \atop S \cdot SO_2 \cdot OH}$.
dithionic	trithionic	tetrathionic	pentathionic

The oxygen analogues of tri- and tetrathionic acids are:

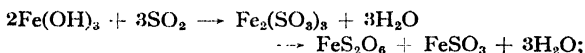
$O \langle {SO_2 \cdot OH \atop SO_2 \cdot OH}$	and	$O \cdot SO_2 \cdot OH$ | $O \cdot SO_2 \cdot OH$,
disulphuric		persulphuric

and just as sulphuric, disulphuric, and persulphuric acids may be regarded as derived from water and hydrogen peroxide by the replacement of hydrogen by the sulphonic group, so the thionic acids may be viewed similarly as derivatives of sulphuretted hydrogen and the persulphides of hydrogen.

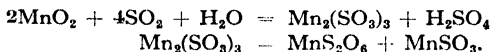
Dithionic acid bears the same relationship to sulphuric acid as oxalic bears to carbonic acid:

$$\underset{\text{sulphuric}}{HO\cdot SO_2\cdot OH} \qquad \underset{\text{carbonic}}{HO\cdot CO\cdot OH}$$

$$\underset{\text{dithionic}}{\begin{array}{c} SO_2\cdot OH \\ | \\ SO_2\cdot OH \end{array}} \qquad \underset{\text{oxalic}}{\begin{array}{c} CO\cdot OH \\ | \\ CO\cdot OH. \end{array}}$$

It is formed by the partial oxidation of sulphurous acid, complete oxidation resulting in the formation of sulphuric acid, thus:

$$2H_2SO_3 + O = H_2S_2O_6 + H_2O$$
$$H_2SO_3 + O = H_2SO_4.$$

When ferric hydroxide reacts with sulphur dioxide in presence of water, ferric sulphite, which is first formed, undergoes self-oxidation and reduction to ferrous dithionate and sulphite, thus:

$$2Fe(OH)_3 + 3SO_2 \longrightarrow Fe_2(SO_3)_3 + 3H_2O$$
$$\longrightarrow FeS_2O_6 + FeSO_3 + 3H_2O;$$

but dithionate is usually prepared by passing sulphur dioxide through water in which manganese dioxide is suspended. The reactions are similar to those with ferric hydroxide, manganic sulphite being first produced, and then yielding manganous dithionate and sulphite thus:

$$2MnO_2 + 4SO_2 + H_2O = Mn_2(SO_3)_3 + H_2SO_4$$
$$Mn_2(SO_3)_3 = MnS_2O_6 + MnSO_3.$$

From the manganous salt the barium salt $BaS_2O_6, 2H_2O$ can be obtained by the addition of baryta solution, and thence the free acid is prepared in solution by decomposing the barium salt with sulphuric acid. On concentrating the solution, however, the acid decomposes thus:

$$H_2S_2O_6 = H_2SO_4 + SO_2.$$

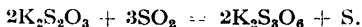
Dithionate is formed by anodic oxidation during electrolysis of a neutral or alkaline solution of sodium sulphite thus:

$$2SO_3^{=} = S_2O_6^{=} + 2E;$$

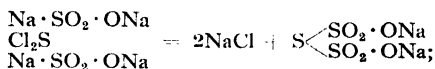
and is reduced in aqueous solution by sodium amalgam, sulphite being regenerated:

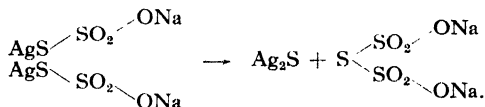
$$Na_2S_2O_6 + 2Na = 2Na_2SO_3.$$

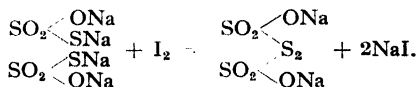
Trithionic acid, $H_2S_3O_6$. Potassium trithionate is formed when sulphur dioxide reacts with a solution of potassium thiosulphate:

$$2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S.$$

The free acid is unstable.

Trithionate may also be obtained by the action of sulphur dichloride on a sulphite, thus:

$$\begin{matrix} Na\cdot SO_2\cdot ONa \\ Cl_2S \\ Na\cdot SO_2\cdot ONa \end{matrix} = 2NaCl + S\begin{matrix} \diagup SO_2\cdot ONa \\ \diagdown SO_2\cdot ONa; \end{matrix}$$

and by heating sodium silver thiosulphate with water:

$$\begin{matrix} AgS\diagup SO_2\diagup ONa \\ AgS\diagdown SO_2\diagdown ONa \end{matrix} \longrightarrow Ag_2S + S\begin{matrix} \diagup SO_2\diagup ONa \\ \diagdown SO_2\diagdown ONa. \end{matrix}$$

Tetrathionic acid.—Sodium tetrathionate is formed in the well-known reaction between sodium thiosulphate and iodine:

$$\begin{matrix} SO_2\begin{matrix} \diagup ONa \\ \diagdown SNa \end{matrix} \\ SO_2\begin{matrix} \diagup SNa \\ \diagdown ONa \end{matrix} \end{matrix} + I_2 = \begin{matrix} SO_2\diagup ONa \\ \diagdown \\ S_2 \\ \diagup \\ SO_2\diagdown ONa \end{matrix} + 2NaI.$$

Ferric chloride reacts in an analogous way with thiosulphate:

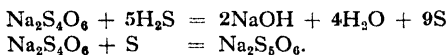
$$2FeCl_3 + 2Na_2S_2O_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6.$$

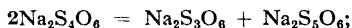
The reaction is reversed by sodium amalgam, thiosulphate being regenerated.

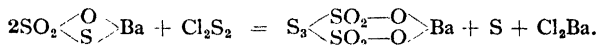
Tetrathionic acid may be obtained in solution by decomposing its barium salt with dilute sulphuric acid. The acid is fairly stable, in solution, but on concentration decomposes thus:

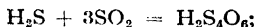
$$H_2S_4O_6 = H_2SO_4 + SO_2 + 2S.$$

Pentathionic acid.—A tetrathionate can combine with nascent sulphur to form pentathionate, and the following reactions take place when hydrogen sulphide is passed into a solution of sodium tetrathionate:

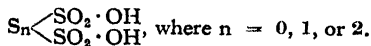
$$Na_2S_4O_6 + 5H_2S = 2NaOH + 4H_2O + 9S$$
$$Na_2S_4O_6 + S = Na_2S_5O_6.$$

Pentathionate is also formed together with trithionate by the spontaneous decomposition of a solution of tetrathionate,

$$2Na_2S_4O_6 = Na_2S_3O_6 + Na_2S_5O_6;$$

and by the action of sulphur chloride on barium thiosulphate,

$$2SO_2{<}{\begin{matrix}O\\S\end{matrix}}{>}Ba + Cl_2S_2 = S_3{<}{\begin{matrix}SO_2-O\\SO_2-O\end{matrix}}{>}Ba + S + Cl_2Ba.$$

Salts of this acid are, however, generally obtained from **Wackenroder's solution**, the liquid formed by passing hydrogen sulphide into strong sulphurous-acid solution at 0°. Although the final products of the interaction of sulphuretted hydrogen and sulphur dioxide are sulphur and water, that result is preceded by the formation of polythionic acids, the first of which is probably tetrathionic acid,

$$H_2S + 3SO_2 = H_2S_4O_6;$$

thence by secondary reactions tri- and pentathionic acids result; and from the solution the alkali salt of the latter acid can be isolated by a lengthy process.

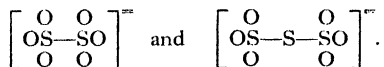
Constitution of the thionic acids.—The formation of di-, tri-, and tetrathionic acids by the reactions of condensation which have been studied above, and the reversal of these reactions by sodium amalgam, are explained by representing the acids by the general formula:

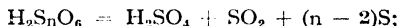
$$S_n{<}{\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix}}, \text{ where } n = 0, 1, \text{ or } 2.$$

Pentathionic acid may be supposed to be similarly constituted, in which case n = 3.

The reactions with iodine and sodium amalgam were studied

by Spring, and the above conclusions as regards constitution have been adopted by Mendeléeff and Blomstrand.

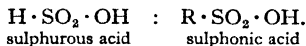
Examination of crystal structure confirms the formulation of the di- and tri-thionate ions as

$$\left[\begin{matrix} & O & & O & \\ O & S & — & S & O \\ & O & & O & \end{matrix}\right]^{=} \quad \text{and} \quad \left[\begin{matrix} & O & & & & O & \\ O & S & — & S & — & S & O \\ & O & & & & O & \end{matrix}\right]^{=}.$$

The following **comparative reactions of thionic acids** may be mentioned. Aqueous solutions of all the acids decompose on concentration according to the reaction:

$$H_2S_nO_6 = H_2SO_4 + SO_2 + (n - 2)S;$$

the solid salts decompose in analogous fashion on heating. Dithionic acid, since its molecule contains but two atoms of sulphur, yields no sulphur on decomposition. Tetrathionic is the most stable of these acids. The barium salts are all soluble in water, but mercurous nitrate gives with trithionate solution a black precipitate and with tetra- and pentathionate solutions yellow precipitates. On warming with copper-sulphate solution, trithionate gives a black precipitate. Easy decomposition by bases is characteristic of pentathionates.

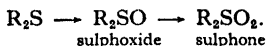
Certain types of organic compounds containing sulphur may here be mentioned.

Sulphonic acids, as previously observed, are derivatives of unsymmetrical sulphurous acid:

$$\underset{\text{sulphurous acid}}{H\cdot SO_2\cdot OH} \; : \; \underset{\text{sulphonic acid}}{R\cdot SO_2\cdot OH.}$$

Sulphinic acids are related to the unsymmetrical form of sulphoxylic acid H_2SO_2:

$$\underset{\text{sulphinic acid}}{R\cdot SO\cdot OH.}$$

Sulphoxides and **sulphones** are formed by the oxidation of sulphides; thus:

$$R_2S \longrightarrow \underset{\text{sulphoxide}}{R_2SO} \longrightarrow \underset{\text{sulphone}}{R_2SO_2.}$$

Sulphonium bases, SR_3OH, and their salts, such as triethyl

sulphonium iodide, $[(C_2H_5)_3S]I$, are related to SH_2, as ammonium bases and their salts to NH_3. The alkyl sulphonium halides are formed by the combination of alkyl sulphides and alkyl halides; thus:

$$(C_2H_5)_2S + C_2H_5I = [(C_2H_5)_3S]I,$$

which is analogous to the reaction:

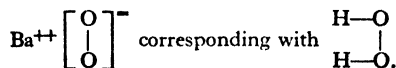
$$(C_2H_5)_3N + C_2H_5I \quad [(C_2H_5)_4N]I.$$

Asymmetric sulphonium salts of the type $[R_1R_2R_3S]A$ have been resolved into optically active components by Pope and Peachey,* and by Smiles.† The activity of the asymmetric ion $[R_1R_2R_3S]^+$ is attributed to tetrahedral disposition of the sulphur valencies, even although one electron pair is unused.

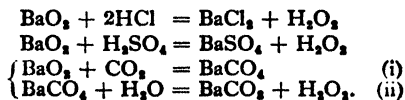
APPENDIX TO SUB-GROUP VI B

Hydrogen Peroxide and the Peracids

As was mentioned in the chapter on oxides, the peroxides may be divided into two classes: the poly-oxides, containing several doubly-linked oxygen atoms, and the superoxides, which contain oxygen chains, such as:

$$Ba^{++}\begin{bmatrix} O \\ | \\ O \end{bmatrix}^{-} \text{ corresponding with } \begin{matrix} H—O \\ \quad | \\ H—O. \end{matrix}$$

Hydrogen Peroxide, H_2O_2.—Barium and sodium peroxides are the usual sources of hydrogen peroxide, though this compound may also be obtained by the electrolytic oxidation of diluted sulphuric acid, a process which involves the formation of persulphuric acids and their subsequent hydrolysis.

The following are the reactions by which H_2O_2 is obtained from BaO_2:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
$$\begin{cases} BaO_2 + CO_2 = BaCO_4 & \text{(i)} \\ BaCO_4 + H_2O = BaCO_3 + H_2O_2. & \text{(ii)} \end{cases}$$

* *Chem. Soc. Trans.* (1900), **77**, 1072.
† *Chem. Soc. Trans.* (1900), **77**, 1174.

The reactions with carbon dioxide are interesting. When this gas is passed into ice-cold water in which barium peroxide is suspended, whilst the liquid is continuously agitated, no hydrogen peroxide is produced for a time, during the formation of percarbonate; then the liquid becomes acid and the percarbonate formed is hydrolyzed according to reaction (ii).

From sodium peroxide hydrogen peroxide is produced by the action of water alone:

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2;$$

but much decomposition of the latter takes place, with evolution of oxygen, because it is not stable in presence of alkali. In presence of acid, however, and particularly at low temperature, hydrogen peroxide is much more stable. Thus a commercial process (Merck) consists in adding sodium peroxide to ice-cold 20 per cent sulphuric acid, and distilling the product *in vacuo*, after the removal of Na_2SO_4, $10H_2O$, which crystallizes. The product is 30 per cent hydrogen peroxide, or **perhydrol**, which on decomposition yields one hundred times its volume of oxygen.

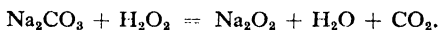
A difficulty in the way of preparing and concentrating hydrogen peroxide is the spontaneous decomposition of this substance in presence of certain catalysts. Thus, when the peroxide is being prepared by the action of carbon dioxide on commercial barium peroxide, some of it is lost in this way before it can be filtered from the barium carbonate, owing to a trace of manganese dioxide derived from manganese in the barium peroxide.

Finely divided and colloidal metals also decompose hydrogen peroxide catalytically, as well as rough glass surfaces. On this account a concentrated solution of the peroxide is sometimes preserved in bottles coated inside with paraffin wax.

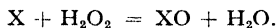
Nearly pure hydrogen peroxide can be obtained by repeated fractionation of its aqueous solution under reduced pressure, and the anhydrous solid by freezing. Pure hydrogen peroxide is a colourless, syrupy, acid liquid of density 1·458 at 0°,

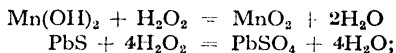
boiling at 69·2° under 26 mm. pressure, and forming columnar prismatic crystals which melt at −2°. Contact with certain catalysts and oxidizable substances causes explosive decomposition. Besides its catalytic decomposition hydrogen peroxide reacts in three different ways:

(i) *Salt formation:*

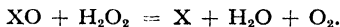
$$Na_2CO_3 + H_2O_2 = Na_2O_2 + H_2O + CO_2.$$

This reaction is brought about by adding sodium-carbonate solution drop by drop to hydrogen-peroxide solution. Thus hydrogen peroxide is an acid, of which superoxides such as BaO_2 and Na_2O_2 are normal salts.

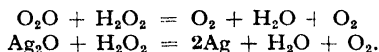
(ii) *Oxidizing action:*

$$X + H_2O_2 = XO + H_2O.$$

Whether oxidation by hydrogen peroxide occurs depends on whether conditions of stability of the oxidation product obtain. The presence of alkali, or at least the absence of acid, generally promotes oxidation, e.g.:

$$Mn(OH)_2 + H_2O_2 = MnO_2 + 2H_2O$$
$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O;$$

though peracids, e.g. pertitanic, pervanadic, and perchromic acids, can be formed in presence of acid.

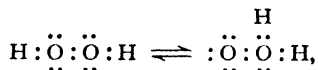
(iii) *Reducing action:*

$$XO + H_2O_2 = X + H_2O + O_2.$$

It appears that reduction by hydrogen peroxide involves evolution of oxygen gas, the substance reduced containing, like hydrogen peroxide, loosely-held oxygen atoms, which in partnership produce molecular oxygen. Examples of this action are:

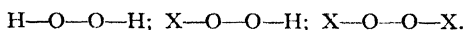
$$O_2O + H_2O_2 = O_2 + H_2O + O_2$$
$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

Presence of acid promotes such reduction, when a salt may be formed thus:

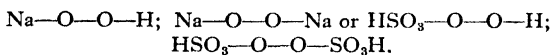
$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$$
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Constitution.—Cryoscopic determination proves that the molecule of hydrogen peroxide is H_2O_2. The compound may be tautomeric, and may be represented electronically in two ways thus:

$$\mathrm{H:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:H \rightleftharpoons :\underset{\cdot\cdot}{\ddot{O}}:\overset{H}{\underset{\cdot\cdot}{\ddot{O}}}:H,}$$

the second formula indicating an acidic character induced in a molecule of water by the second atom of oxygen; this atom might be readily lost. According to G. H. Geib (1932) another form of hydrogen peroxide results when atomic hydrogen reacts with oxygen at very low temperatures. This new form changes at $-115°$ to the ordinary form with some decomposition into water and oxygen. Hydrogen peroxide is generally formulated as H—O—O—H.

The Peracids.—Hydrogen peroxide may give rise to two classes of derivatives in which one or both hydrogen atoms are replaced by univalent atoms or groups thus:

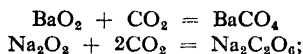
H—O—O—H; X—O—O—H; X—O—O—X.

The atom or radicle X may be basic or acidic; thus, for example:

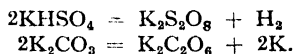
Na—O—O—H; Na—O—O—Na or HSO_3—O—O—H;
HSO_3—O—O—SO_3H.

These simple principles underlie the whole of the chemistry of the peracids and their salts.

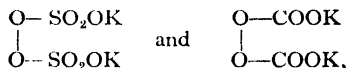
Formation of peracids and salts.—In general, two methods are available for the formation of peracids and their salts: first, by the use of hydrogen peroxide or its simple metallic derivatives such as Na_2O_2 or BaO_2; second, by electrolytic oxidation or, more strictly speaking, anodic condensation. And, as will appear below, persalts formed by electrolysis possess a constitution such as is not assumed by such salts formed from peroxides.

As examples of the first method may be quoted the produc-

tion of barium percarbonate, $BaCO_4$, or sodium percarbonate, $Na_2C_2O_6$, from BaO_2 or Na_2O_2 and carbon dioxide thus:

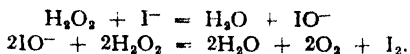
$$BaO_2 + CO_2 = BaCO_4$$
$$Na_2O_2 + 2CO_2 = Na_2C_2O_6;$$

whilst examples of the second method are furnished by the formation of potassium persulphate and percarbonate by electrolysis thus:

$$2KHSO_4 = K_2S_2O_8 + H_2$$
$$2K_2CO_3 = K_2C_2O_6 + 2K.$$

Persalts of the first kind possess a constitution related to that of the peroxides from which they are derived. Thus $BaCO_4$, formed from BaO_2 and CO_2, is $Ba\begin{matrix} / O - O \\ \quad \quad | \\ \backslash O - C = O \end{matrix}$, and $Na_2C_2O_6$, formed from Na_2O_2 and $2CO_2$, is NaO—O—OC—O—COONa; whilst $K_2S_2O_8$ and $K_2C_2O_6$, formed by electrolysis, are:

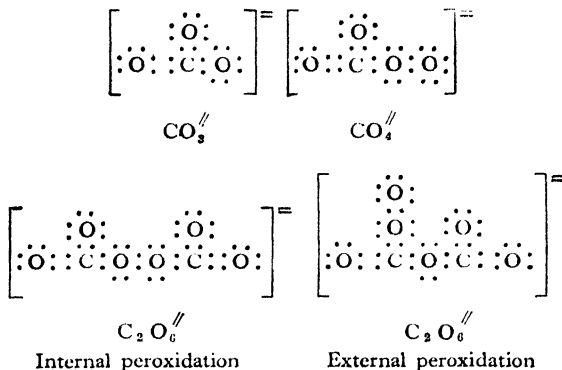
$$\begin{matrix} O-SO_2OK \\ | \\ O-SO_2OK \end{matrix} \quad \text{and} \quad \begin{matrix} O-COOK \\ | \\ O-COOK, \end{matrix}$$

respectively. There is, indeed, a form of $K_2C_2O_6$, isomeric with the above, prepared from potassium peroxide, which resembles in constitution the above sodium salt, similarly prepared.

The essential difference between these two kinds of persalts is in the positions of the oxygen grouping —O—O—. In electrolytic persalts this grouping is internal, i.e. between the two sulphur or carbon atoms in the examples given; whilst in salts prepared from peroxides it is external to the acidic nucleus, as the above formula for sodium percarbonate shows. This difference of constitution is indicated by difference of reactivity towards potassium iodide.

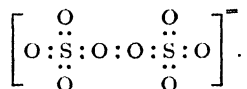
In some cases it is difficult to distinguish true peroxy-compounds from salts containing hydrogen peroxide of crystallization, which, like H_2O_2 itself, react slowly with KI solution.

$$H_2O_2 + I^- = H_2O + IO^-$$
$$2IO^- + 2H_2O_2 = 2H_2O + 2O_2 + I_2.$$

According to Liebhafsky (1934), true peroxy-compounds liberate iodine continuously from buffered potassium iodide solutions, whilst, in the other type, the initial liberation of iodine is soon replaced by oxygen evolution.

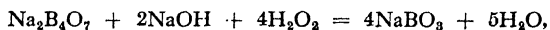
The carbonate, permonocarbonate, and perdicarbonate ions are represented electronically thus:

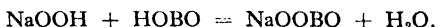
```
 [      ..       ]=   [      ..          ]=
 [     :O:       ]    [     :O:          ]
 [ ..   ..  ..   ]    [ ..  ..  ..  ..   ]
 [:O: :C: O:     ]    [:O::C :O :O:      ]
 [        ..     ]    [      ..  ..      ]

        CO3''                 CO4''

 [     ..      ..         ]=   [        ..          ]=
 [    :O:     :O:         ]    [       :O:          ]
 [ ..  ..  ..  ..  ..  .. ]    [        ..   ..     ]
 [:O: :C :O :O :C: :O:    ]    [       :O:  :O:     ]
 [        ..  ..          ]    [ ..  ..  ..  ..  .. ]
                               [:O: :C :O :C: :O:   ]
                               [          ..        ]

        C2O6''                        C2O6''
 Internal peroxidation        External peroxidation
```

The last formula suggests that a second oxygen atom might be peroxidized, producing the ion C_2O_7''; and it even seems possible that internal and external peroxidation might occur simultaneously, producing in a maximum state of peroxidation the ion C_2O_8''.

Crystal analysis of $(NH_4)_2S_2O_8$ confirms internal peroxidation in the ion $S_2O_8^=$, thus:

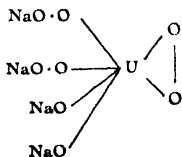
```
 [     O       O    ]=
 [     ..      ..   ]
 [ O : S : O : O : S : O ] .
 [     ..      ..   ]
 [     O       O    ]
```

Most of the peracids and their salts have been prepared, not by electrolysis but from peroxides. Such acids are formed by the combination of normal acids with hydrogen peroxide,

as for example the yellow peroxy-acid formed when hydrogen peroxide and TiO_2 react in sulphuric acid solution. Peruranic acid, which has the empirical composition UO_4, $2H_2O$, and is probably $(HO)_4U\langle{}^{O}_{O}|$, is precipitated when hydrogen peroxide is added to a slightly acid solution of uranyl nitrate. Persalts, corresponding with such peracids, are formed by the combination of metallic peroxides, or hydrogen peroxide in presence of alkali, with normal acids, or sometimes with peracids; in the latter case both base and acid contribute peroxidized qualities to the salt. The perborate $NaBO_3$ is formed thus:

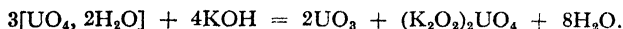
$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 = 4NaBO_3 + 5H_2O,$$

and also by the reaction:

$$NaOOH + HOBO = NaOOBO + H_2O.$$

This reaction may be regarded as the neutralization of metaboric acid by the peroxidized base sodium hydroperoxide, which bears the same relation to Na_2O_2 as NaOH bears to Na_2O. Potassium hyperborate KBO_4, H_2O, however, is peroxidized from both basic and acidic sources of the salt, and appears to have the constitution $K^+\left[:\ddot{O}:\ddot{O}:B::\ddot{O}:\ddot{O}:\right]^-$.

Combination between basic peroxides or hydroperoxides and peracids yields highly peroxidized salts. Thus the action of hydrogen peroxide on alkaline sodium uranate produces the salt $(Na_2O_2)_2$, UO_4, $8H_2O$, which is hydrolyzed by aluminium hydroxide yielding sodium hydroperoxide and peruranic acid, and therefore is constituted thus:

NaO·O
NaO·O — U (O—O)
NaO
NaO

so that one-third of the peroxidic oxygen is associated with the acid and two-thirds with the base. Persalts, such as the above, which are derived from hydrogen peroxide, yield this substance when decomposed by dilute sulphuric acid.

With potassium hydroxide peruranic acid reacts thus:

$$3[UO_4, 2H_2O] + 4KOH = 2UO_3 + (K_2O_2)_2UO_4 + 8H_2O.$$

In this reaction the potash is peroxidized by some of the peruranic acid, and then unites with more of this acid to form the doubly peroxidized salt.

Peracids and their salts are formed by elements in various groups of the Periodic System as follows:

Group III.—B.
,, IV.—C, Ti, Zr, Th; Ge, Sn.
,, V.—N, P; V, Cb, Ta.
,, VI.—S, Se; Cr, Mo, W, U.
(see p. 398).

Sulphur Heptoxide and the Persulphuric Acids

The acidic superoxide, **sulphur heptoxide,** S_2O_7, is said to be formed by the union of sulphur dioxide and oxygen under the influence of a silent electric discharge, the volatile unstable product (M.P. 0° C.) yielding persulphuric acid with water. It is perhaps a mixture, SO_3, SO_4 (Meyer, 1922). According to R. Schwarz (1934), **sulphur tetroxide,** SO_4, is obtained as a white solid (M.P. 3°) under somewhat similar conditions. It is also formed (Fichter, 1927) when fluorine acts on sulphuric acid (2·3 M). It does not yield permonosulphuric acid with water, and is distinguished therefrom by oxidizing manganous salts to permanganate, and aniline to nitrobenzene.

The Persulphuric Acids

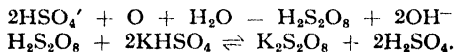
Permonosulphuric acid, Caro's acid, H_2SO_5; $HO{\cdot}SO_2{\cdot}O{\cdot}OH$.
Perdisulphuric acid, $H_2S_2O_8$; $HO{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH$.

The latter of these two acids was the first to be discovered,

Peracids.	Characteristic Salts.
Boron —	$NaO{\cdot}O{\cdot}B:O$; $KO{\cdot}O{\cdot}B:O{\cdot}O$.
Carbon —	Na_2CO_4, $K_2C_2O_6$ $\begin{cases}KOOC{\cdot}O{\cdot}O{\cdot}COOK\\KO{\cdot}O{\cdot}OC{\cdot}O{\cdot}COOK.\end{cases}$
Titanium $(HO)_2Ti<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$, $2H_2O$, or $Ti\begin{smallmatrix}\diagup O{\cdot}OH\\\diagdown(OH)_3\end{smallmatrix}$, H_2O	$\begin{smallmatrix}NaO{\cdot}O\\NaO\end{smallmatrix}>Ti<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$, $3H_2O$.
Zirconium $Zr\begin{smallmatrix}\diagup O{\cdot}OH\\\diagdown(OH)_3\end{smallmatrix}$	$Na_4Zr_2O_{11}$, $9H_2O$.
Tin $HSnO_4$, $2H_2O$; $H_2Sn_2O_7$, $3H_2O$	$KSnO_4$, $2H_2O$; $K_2Sn_2O_7$, $3H_2O$.
Nitrogen $O_2N{\cdot}O{\cdot}OH$	Ag_7NO_{11}, KNO_4 (?).
Phosphorus $PO(OH)_2{\cdot}O{\cdot}OH$	$PO(ONa)(OONa)_2$, $6\frac{1}{2}H_2O$, or Na_3PO_4, $2H_2O_2$, $4\frac{1}{2}H_2O$.
Vanadium $HOVO<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$	KVO_4, KVO_5, K_3VO_8, $2\frac{1}{2}H_2O$.
Columbium $HOCbO<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$	$KCbO_4$, $(KOO)_3Cb<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$.
Tantalum $HOTaO<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$, nH_2O	$NaTaO_4$, $NaTaO_5$, $(MOO)_3Ta<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$.
Sulphur $HOSO_2{\cdot}O{\cdot}O{\cdot}SO_2OH$, $HO{\cdot}OSO_2OH$	$K_2S_2O_8$, $KHSO_5$.
Selenium —	$K_2Se_2O_8$ (?).
Chromium H_3CrO_8, $2H_2O$, i.e. $(HO)_4Cr(OOH)_3$	$(NH_4)_3CrO_8$ (red), i.e. $CrO_2(OONH_4)_3$; $NH_4H_2CrO_7$ (blue), i.e. NH_4CrO_5, H_2O_2.
Molybdenum H_2MoO_5, i.e. $(HO)_2MoO<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$; H_2MoO_6, i.e. $\begin{smallmatrix}HOO\\HO\end{smallmatrix}>MoO<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$	$(KO{\cdot}O)_2MoO<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$.
Tungsten $H_2WO_5(WO_3, H_2O_2)$; $H_4WO_7(WO_3, 2H_2O_2)$	$Na_2W_2O_8$, i.e. $NaOWO_2{\cdot}O{\cdot}O{\cdot}WO_2ONa$; $Na_2W_2O_9$, i.e. $NaOWO{-}O{-}WOONa$ (each W bridged by $O{-}O$).
Uranium UO_4, $2H_2O$, i.e. $(HO)_4U<\begin{smallmatrix}O\\\mid\\O\end{smallmatrix}$	$(Na_2O_2)_2UO_4$, $8H_2O$.

and is generally the source of the former; it will therefore be described first.

Perdisulphuric acid.—Potassium perdisulphate, or more simply persulphate, was first obtained by Marshall * by the electrolysis of potassium hydrogen sulphate with high current density at the anode, oxidation occurring thus:

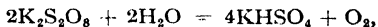
$$2HSO_4' + O + H_2O = H_2S_2O_8 + 2OH^-$$
$$H_2S_2O_8 + 2KHSO_4 \rightleftharpoons K_2S_2O_8 + 2H_2SO_4.$$

Since this change consists of the union in pairs of the anions HSO_4, and the crystallization of the sparingly soluble potassium salt of the acid $H_2S_2O_8$, the oxygen grouping —O—O— is necessarily internal to the two sulphur atoms, an arrangement on which the specific oxidizing properties of perdisulphates depend. The acid $H_2S_2O_8$ is thus a derivative of H_2O_2 in which both hydrogen atoms are replaced by sulphonic acid groups, SO_3H.

Perdisulphuric acid itself has been obtained by the interaction of well-cooled chlorosulphonic acid and anhydrous hydrogen peroxide† thus:

$$2Cl \cdot SO_3H + H_2O_2 = (O \cdot SO_3H)_2 + 2HCl;$$

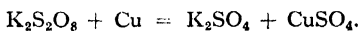
and forms hygroscopic crystals melting at about 65°, which when pure may be kept for months without decomposition.

Reactions of persulphates.—An aqueous solution of potassium persulphate decomposes slowly when cold, more quickly when boiling, according to the following reaction:

$$2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2,$$

and the salt may be estimated by titrating the acid produced. Chlorides, bromides, and iodides are oxidized by persulphate with liberation of halogen, the speed of liberation of iodine being accelerated catalytically by ferrous sulphate. From salts of silver, copper, manganese, and cobalt the higher oxides

* *Chem. Soc. Trans.* (1891), **59**, 771.
† D'Ans and Friederich, *Ber.* (1910), **43**, 1880.

are precipitated, and minute quantities of manganese in acid solution are converted completely into permanganate by persulphate in presence of silver nitrate as catalyst. Ferrous salt is quickly converted into ferric by persulphate, and this reaction furnishes a second method of estimating persulphate if the excess of ferrous iron is titrated with permanganate. Certain metals are dissolved by persulphate, without evolution of gas, e.g. copper, thus:

$$K_2S_2O_8 + Cu = K_2SO_4 + CuSO_4.$$

Persulphate reacts but slowly with hydrogen peroxide, and it is distinguished from this substance by not decolorizing permanganate, and by giving no yellow colour with titanic salt or blue colour with chromic acid.

Permonosulphuric acid, Caro's acid.—In 1898 Caro* found that when ammonium or potassium persulphate is added to concentrated sulphuric acid, and the solution after a few minutes is poured into water, the addition of aniline does not yield aniline black, as it does with persulphuric acid itself, but that on neutralization with ammonium carbonate a green colour and a precipitate of nitrosobenzene, C_6H_5NO, result. The new acid thus produced Baeyer and Villiger† called *Caro's acid*, and attributed to it the formula H_2SO_5. This acid may be conveniently obtained free from sulphuric acid and hydrogen peroxide, but containing some unchanged persulphuric acid, by pouring the sulphuric acid solution of persulphate on to crushed ice, and then adding to the solution thus diluted excess of barium phosphate.

Caro's acid can be produced in three ways:

(i) Action of concentrated sulphuric acid on $K_2S_2O_8$.

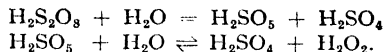
(ii) Electrolysis of sulphuric acid of density 1·45.

(iii) Interaction of concentrated sulphuric acid and hydrogen peroxide.

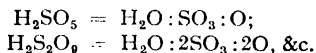
It has already been seen that in method (i) permonosulphuric

* *Zeitsch. angew. Chemie* (1898), **11**, 845.
† Baeyer and Villiger, *Ber.* (1901), **34**, 853.

acid is formed by the decomposition of perdisulphuric acid; similarly in method (ii), the perdiacid is first produced by anodic condensation of SO_4H' ions, and then hydrolysed to form permonosulphuric acid, thus:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \rightleftharpoons H_2SO_4 + H_2O_2.$$

The reversibility of the second reaction illustrates the production of Caro's acid by method (iii). On the other hand, the hydrolysis is completed if the hydrogen peroxide be distilled in vacuo; in this way the technical production of H_2O_2 from perdisulphuric acid is possible.

Constitution of permonosulphuric acid.—Permonosulphuric acid is distinguished from hydrogen peroxide by not reacting with acidified permanganate, and from perdisulphuric acid by quickly liberating iodine from potassium iodide. By the latter reaction the ratio of active oxygen to SO_3 was found by Baeyer and Villiger to be as 1 to 1. According to this result the acid might have one of alternative formulæ for:

$$H_2SO_5 = H_2O:SO_3:O;$$
$$H_2S_2O_9 = H_2O:2SO_3:2O, \text{ \&c.}$$

The latter formula appeared to Armstrong and Lowry * to be preferable, for the solution of a neutral salt of Caro's acid becomes acid by loss of oxygen on boiling, which appears to be a property of $K_2S_2O_9$ rather than of K_2SO_5, thus:

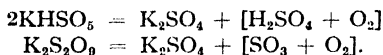
$$K_2SO_5 = K_2SO_4 + O$$
$$K_2S_2O_9 + H_2O = K_2SO_4 + H_2SO_4 + O_2.$$

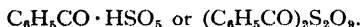
But if Caro's acid should be monobasic, and its potassium salt be $KHSO_5$, this salt would become acid by loss of oxygen thus:

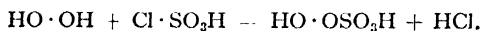
$$2KHSO_5 = 2KHSO_4 + O_2.$$

* *Roy. Soc. Proc.* (1902), **70**, 94.

Slater Price* decided in favour of the latter view by reason of the loss which a mixture of potassium salts, containing a known proportion of permonosulphate, underwent on ignition; for $2KHSO_5$ will lose on ignition more than $K_2S_2O_8$, as the following equations show:

$$2KHSO_5 = K_2SO_4 + [H_2SO_4 + O_2]$$
$$K_2S_2O_8 = K_2SO_4 + [SO_3 + O_2].$$

This conclusion is confirmed by the preparation of a benzoyl derivative† which might be:

$$C_6H_5CO \cdot HSO_5 \text{ or } (C_6H_5CO)_2S_2O_8.$$

Since the benzoylated product is still an acid with a hydrogen atom replaceable by potassium, the first formula is correct, and Caro's acid is H_2SO_5, being monobasic. The pure acid has been obtained as a crystalline solid, melting at 45°, by the interaction of anhydrous hydrogen peroxide and chlorosulphonic acid in molecular proportions thus:‡

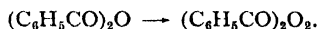
$$HO \cdot OH + Cl \cdot SO_3H = HO \cdot OSO_3H + HCl.$$

Permonosulphuric acid possesses specific oxidizing powers, of value in the study of organic compounds. For instance, primary aromatic amines are oxidized to nitroso-compounds,

$$RNH_2 \longrightarrow RNO,$$

tertiary fatty-aromatic amines to oxyamines,

$$C_6H_5(CH_3)_2N \longrightarrow C_6H_5(CH_3)_2NO,$$

and anhydrides of acids to peranhydrides, e.g.;

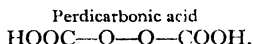
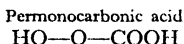
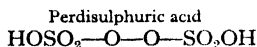
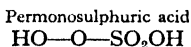
$$(C_6H_5CO)_2O \longrightarrow (C_6H_5CO)_2O_2.$$

* *Chem. Soc. Trans.* (1906), **89**, 53.

† Willstätter and Hauenstein, *Ber.* (1909), **42**, 1839.

‡ D'Ans and Friederich, *Ber.* (1910), **43**, 1880.

Percarbonates and Perchromates

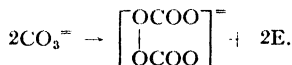
Percarbonates.—According to analogy with permono- and perdisulphuric acids two percarbonic acids may be expected to exist, thus:

Permonosulphuric acid	Perdisulphuric acid
$HO—O—SO_2OH$	$HOSO_2—O—O—SO_2OH$
Permonocarbonic acid	Perdicarbonic acid
$HO—O—COOH$	$HOOC—O—O—COOH$.

This expectation is realized, and indeed the following peroxidized carbonates have been obtained:

(i) *Carbonates*, containing hydrogen peroxide of crystallization, e.g. $2Na_2CO_3$, $3H_2O_2$, which in oxidizing action are similar to hydrogen peroxide itself.

(ii) *Permonocarbonates*, e.g. Na_2CO_4 and $BaCO_4$, obtained by the combination of Na_2O_2 and BaO_2 with carbon dioxide without previous liberation of H_2O_2.

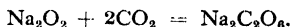
(iii) *Perdicarbonates*, e.g. $K_2C_2O_6$, obtained like perdisulphates, by electrolysis, using K_2CO_3, thus:

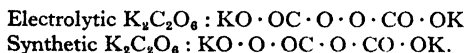
$$2CO_3^{=} \rightarrow \begin{bmatrix} OCOO \\ | \\ OCOO \end{bmatrix}^{=} + 2E.$$

These salts liberate iodine immediately and quantitatively from cold, neutral, potassium-iodide solution thus:

$$C_2O_6'' + 2I' = 2CO_3'' + I_2,$$

and are so distinguished from hydrogen peroxide.

(iv) *Perdicarbonates*, $Na_2C_2O_6$ and $K_2C_2O_6$, isomeric with the above, have also been obtained from sodium and potassium peroxide and carbon dioxide thus:

$$Na_2O_2 + 2CO_2 = Na_2C_2O_6.$$

These salts differ in their behaviour with potassium iodide from electrolytic perdicarbonates, and are believed to be related to the electrolytic salts thus:

Electrolytic $K_2C_2O_6$: $KO \cdot OC \cdot O \cdot O \cdot CO \cdot OK$
Synthetic $K_2C_2O_6$: $KO \cdot O \cdot OC \cdot O \cdot CO \cdot OK$.

Perchromates.—In the familiar "perchromic acid" test for chromium, hydrogen peroxide added to an acidified chromate solution forms a deep-blue, ether-soluble oxide, CrO_5. Organic bases such as triethylamine or pyridine, when added to the ethereal solution, form blue compounds which were formerly regarded as salts of a perchromic acid, $HCrO_5$, but are now formulated as co-ordination complexes, the pyridine compound being $C_5H_5N \rightarrow CrO_5$. Presumably the oxide is stabilized in ether solution as the complex, $(CH_3)_2O \rightarrow CrO_5$.

The addition of alcoholic solutions of alkalis to the blue ether solution forms solid, blue, unstable perchromates such as $K_2Cr_2O_{12}$, $2H_2O$. The existence of an analogous anhydrous thallous salt, $Tl_2Cr_2O_{12}$, confirms that the potassium salt is a hydrate and not a perhydrate.

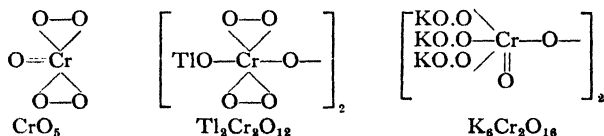
With chromic acid in cold alkali solutions hydrogen peroxide forms the red perchromates, $M_6Cr_2O_{16}$, whose solutions, on acidification, evolve oxygen and yield the blue ether-soluble compound.

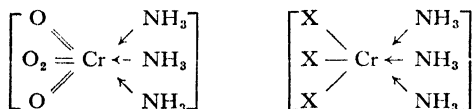
Finally, chromium tetroxide triammine, CrO_4, $3NH_3$, is formed as brown needles when 30 per cent hydrogen peroxide is added to cold ammoniacal solutions of chromic acid.

The blue and red salts were formerly considered to be, respectively, $MCrO_6$ and M_3CrO_8, but their dimeric character is established by the work of Schwarz and Giese (1933), who found that the active oxygen could be estimated by potassium permanganate, using ammonium molybdate as a catalyst.

They showed that these salts contain, respectively, 2·5 and 3·5 peroxo-groups (—O—O—) per atom of chromium. Hence these compounds contain sexivalent chromium as shown below, and not septivalent chromium as in the older formulæ.

```
  O—O            ┌    O—O      ┐      ┌KO.O\              ┐
   \/            │     \/      │      │KO.O—Cr—O—         │
O=Cr             │TlO—Cr—O—    │      │KO.O/ ||           │
   /\            │     /\      │      │       O           │
  O—O            └    O—O      ┘2     └                   ┘2
 CrO5              Tl2Cr2O12                K6Cr2O16
```

CrO_5 $Tl_2Cr_2O_{12}$ $K_6Cr_2O_{16}$

Chromium tetroxide triammine, $CrO_4 \cdot 3NH_3$, is represented like the non-electrolytic ammine $CrX_3 \cdot 3NH_3$, thus:

$$\left[\begin{array}{ccccc} O & & & & NH_3 \\ & \searrow\!\!\searrow & & \swarrow & \\ O_2 & = & Cr & \leftarrow & NH_3 \\ & \nearrow\!\!\nearrow & & \nwarrow & \\ O & & & & NH_3 \end{array}\right] \qquad \left[\begin{array}{ccccc} X & & & & NH_3 \\ & \diagdown & & \swarrow & \\ X & - & Cr & \leftarrow & NH_3 \\ & \diagup & & \nwarrow & \\ X & & & & NH_3 \end{array}\right]$$

SUB-GROUP VI A

Chromium, Molybdenum, Tungsten, and Uranium

As indicated in the introduction to Group VI, these elements, constituting a group of metals, do not display any close analogies with their congeners of sub-group VI B, except in the formation of the acidic trioxides MO_3.

In its chief basic oxide, Cr_2O_3, chromium is allied to aluminium and iron; thus, like aluminium hydroxide, chromic hydroxide, $Cr(OH)_3$, is able to form salts with alkalis, the chromites, which are, however, considerably less stable than the aluminates, undergoing decomposition when their solutions are heated. Chromic sulphate, also, like the sulphates of aluminium and ferric iron, gives rise to alums.

These **metals** are not found native, but occur as oxides, such as Cr_2O_3, in chrome ironstone, and U_3O_8, pitchblende; as sulphides, such as MoS_2; and as salts of the H_2MO_4 acids, like $PbCrO_4$, $PbMoO_4$, and $CaWO_4$.

They are prepared by the reduction of their oxides or chlorides by means of carbon, potassium cyanide, hydrogen, sodium, or aluminium;* and they are all metals of high melting-point and low atomic volume.

They combine directly on heating with oxygen, and with the halogens, forming with chlorine the volatile chlorides $CrCl_3$, $MoCl_5$, WCl_6, UCl_4, of which WCl_6 easily dissociates at temperatures slightly above its boiling-point into WCl_5 and chlorine.

* The Goldschmidt process consists in firing a mixture of the oxide (Fe_2O_3, Cr_2O_3, &c.) with aluminium powder by means of a suitable fuse. Owing to the great heat developed the process has been used in the welding of iron rails.

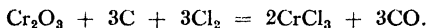
Halides

The halides are of numerous types, as will be seen from the table:

	Fluorides	Chlorides	Bromides	Iodides
Chromium	CrF_2, CrF_3	$CrCl_2$, $CrCl_3$	$CrBr_2$, $CrBr_3$,	CrI_2, CrI_3
Molybdenum ..	MoF_6	Mo_3Cl_6, $MoCl_3$, $MoCl_4$, $MoCl_5$	$MoBr_2$, $MoBr_3$, $MoBr_4$	MoI_2, MoI_4
Tungsten	WF_6	W_3Cl_6, WCl_4, WCl_5, WCl_6	WBr_2, WBr_5, WBr_6	WI_2, WI_4
Uranium	UF_4, UF_6	UCl_3, UCl_4, UCl_6	UBr_4	UI_4

A large number of oxyhalides are also known.

In addition to their formation by direct union, and by the solution of the metal or oxide in the halogen acid, many of the halides may be prepared by the action of a halogen on a heated mixture of oxide and carbon, as, for example:

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO.$$

The nature of these compounds is manifested:

(i) By behaviour towards water.

(ii) By volatility and solubility in non-hydroxylic solvents.

Chlorides of Molybdenum and Tungsten

The simple dichloride, $MoCl_2$, does not exist, being represented by the amphoteric, trimeric solid, Mo_3Cl_6, or $[Mo_3Cl_4]Cl_2$, since it gives rise to $[Mo_3Cl_4](OH)_2$, $8H_2O$, and $[Mo_3Cl_4](NO_3)_2$. With hydrochloric acid it yields $H[Mo_3Cl_7]$ which forms compounds of the type, $H[Mo_3Cl_4Br_3, H_2O]$, $3H_2O$, and salts $M^{\cdot}[Mo_3Cl_7]$, xH_2O. The chloride, Mo_3Cl_6, results by heating molybdenum in a stream of $COCl_2$, or by thermal decomposition of $MoCl_3$. Tungsten forms similar complex compounds. (Cf. Cb and Ta.)

Molybdenum trichloride is a brown solid sufficiently soluble in water to be hydrolyzed. It forms salts, $R^{\cdot}_3[MoCl_6]$ and yields two isomeric oxychlorides, $[MoOCl, 4H_2O]$.

Tungsten trichloride is represented in the green complex alkali salts, $R^{\cdot}_3[W_2Cl_9]$, which are strong reducing agents.

The tetrachlorides, $MoCl_4$ (crystalline powder), and WCl_4 (infusible grey-brown crystals), are hygroscopic and partially decomposed by water. Both yield the metal on strong heating.

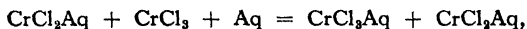
The pentachlorides form black deliquescent crystals decomposed by water to give the blue oxides and hydrochloric acid. $MoCl_5$ (M.P. 194°, B.P. 268°) is soluble in alcohol and ether, WCl_5 (M.P. 248°, B.P. 275·6°) is slightly soluble in carbon disulphide.

Tungsten hexachloride consists of dark violet crystals which are easily volatile, M.P. 275°, B.P. 347°. It is decomposed by boiling water, and is easily soluble in carbon disulphide. Related to it is the oxytetrachloride, $WOCl_4$.

The higher halides of molybdenum and tungsten, and to a less extent of uranium, are noteworthy, as compared with the halides of chromium. In forming hexafluorides these metals resemble sulphur, but in its hexachloride and hexabromide tungsten stands alone, being the only element known to form such halides.

None of these chlorides can be considered a well-defined salt, since they do not manifest definitely saline properties towards water. The volatility and solubility in carbon disulphide of the higher chlorides, as well as the fact that they are decomposed by water into hydrochloric acid and an oxide, show them to be ill-defined chloranhydrides. The existence of numerous oxyhalides illustrates the same fact. The reluctance of molybdenum and tungsten to form true salts in their lower valencies contrasts with the existence of the ions, $Cr^{\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$, with the basicity of uranium in the salt-like compounds, $U(SO_4)_2$ and UCl_4, and the bivalent uranyl ion $(UO_2)^{\cdot\cdot}$. The lower oxides show similar lack of basic character. True basigenic character is shown in the case of chromium by the fact that chromous chloride is a true salt, soluble in water and crystallizing with water of crystallization, while chromic chloride is inert when prepared in the anhydrous condition by heating a mixture of chromic oxide and carbon in a current of chlorine. The presence, however, of a trace of

chromous (cuprous or stannous) chloride effects solution, thus:

$$CrCl_2Aq + CrCl_3 + Aq = CrCl_3Aq + CrCl_2Aq,$$

the $CrCl_2Aq$ being oxidized by the solid $CrCl_3$ to $CrCl_3Aq$, the reduced chloride thus passing into solution as $CrCl_2Aq$. $CrCl_3$ may be obtained from this solution in a soluble crystalline form as $CrCl_3, 6H_2O$.

In this form chromic chloride is analogous to ferric chloride, and may therefore be considered as the chloride of a weak base. Chromic chloride further resembles aluminium and ferric chlorides by forming double salts with alkali chlorides, such as $CrCl_3, 2KCl, 2H_2O$.

Among its congeners, chromium is unique in forming organic derivatives, and well-defined chromammines (q.v.).

For bivalent combination these elements will show an electron structure of the general type; *x*.12.2. By loss of two electrons the ion $Cr^{\cdot\cdot}$ is formed. The anomalous behaviour of molybdenum and tungsten must be ascribed to weak basigenic character, the two electrons being used covalently. The additional electrons required to complete a stable valency group are not derived from the inner quantum group, but are gained co-ordinatively by condensation. The structure of these bivalent compounds is uncertain, but there is some chemical evidence for the formulation of $[Mo_3Cl_4](OH)_2$, $8H_2O$, thus:

$$[Mo_3Cl_4 \,.\, 2H_2O](OH)_2,\ 6H_2O$$

for dehydration by heat yields

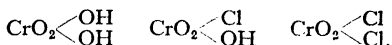
$$[MO_3Cl_4 \,.\, 2H_2O]O.$$

Similar considerations apply to tungsten in the tervalent state, e.g. in the ion $[W_2Cl_9]^{\equiv}$, and it is surprising that the simple dimeric chloride, $(WCl_3)_2$, does not exist. The same tendency to higher co-ordination results in WCl_6, though here the W atom has supplied 6 of the 12 valency electrons.

Chromium forms no higher chlorides, thus further resembling aluminium and iron, and so does not furnish a chloranhydride of an ortho-acid. Like sulphur it forms an oxychloride,

the chloride of a meta-acid, **chromyl chloride,** CrO_2Cl_2. This compound, prepared by heating together potassium dichromate, sodium chloride, and sulphuric acid, is a dark red liquid, boiling at 116°, and is analogous to sulphuryl chloride, SO_2Cl_2. It forms chromic and hydrochloric acids with water; but salts of the intermediate chlorochromic acid, analogous to chlorosulphonic acid, are known, and are formed when concentrated hydrochloric acid acts on a dichromate.

Chromic acid, chlorochromic acid, and chromyl chloride are thus related to one another:

$$CrO_2\langle{}^{OH}_{OH} \qquad CrO_2\langle{}^{Cl}_{OH} \qquad CrO_2\langle{}^{Cl}_{Cl}.$$

It is instructive to observe that while chromyl fluoride, CrO_2F_2, is known, the bromide and iodide are not formed, because chromic acid oxidizes hydrobromic and hydriodic acids.

The oxyhalides of the same type formed by the other metals of the group do not so readily undergo resolution by water; UO_2Cl_2, for instance, is quite stable, and may be regarded as a uranyl salt. The solubility of this latter compound in alcohol and ether, however, and its power of combination with alkali chlorides and the hydrochlorides of organic bases, reveal acidic character.

Oxides

The **oxides of Group VI A** metals are numerous, like the halides. The principal ones are classified in the subjoined table:

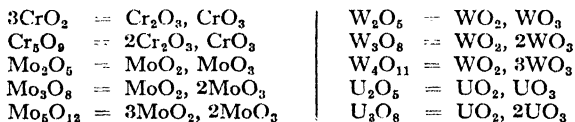
Chromium ..	CrO	Cr_2O_3		CrO_3	$CrO_4(+ 3NH_3)$
Molybdenum ..	MoO (hydrated)	Mo_2O_3	MoO_2	MoO_3	
Tungsten ..	—	—	WO_2 (W_2O_5)	WO_3	
Uranium ..	—	—	UO_2	UO_3	$UO_4, 2H_2O$

Of **oxides** of the **type MO,** examples are known in the case of chromium and molybdenum only. $Cr(OH)_2$ is a true base, dissolving in acids to form the chromous salts; hydrated MoO possesses feebly basic properties. Of the **sesquioxides,** M_2O_3, Cr_2O_3 is a basic oxide possessing feebly acidic properties, Mo_2O_3 shows no acidic properties, and its basic functions are ill defined, since it is insoluble in acids, and even the hydroxide dissolves with difficulty.

Of the **dioxides**, MoO_2 forms very unstable salts; the hydroxide $Mo(OH)_4$ dissolves slowly in water, forming an acid solution. WO_2 is slightly soluble in concentrated hydrochloric and sulphuric acids, forming purple solutions which possibly contain tungstous salts. As was pointed out when dealing with the chlorides, molybdenum and tungsten oxides show a remarkable inability to form salts with acids. UO_2, uranous oxide, corresponds with uranous salts of the type UX_4. Complex derivatives of the unknown oxide W_2O_5, and of the corresponding oxychloride, $WOCl_3$, have been prepared.* The oxides MO_3 are all acidic; but UO_3 is sufficiently basic to form the uranyl salts UO_2X_2.

CrO_4 and UO_4 are peroxides resulting from the action of hydrogen peroxide on chromates and uranates. (See Appendix to Group VI B.)

In addition to the above oxides a number of complex oxides exist, which, in the case of chromium, are compounds of Cr_2O_3 and CrO_3, and, in the case of the other metals, of MO_2 and MO_3. The following are the more important of these complex oxides:—

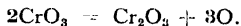
$3CrO_2$	=	Cr_2O_3, CrO_3
Cr_5O_9	=	$2Cr_2O_3, CrO_3$
Mo_2O_5	=	MoO_2, MoO_3
Mo_3O_8	=	$MoO_2, 2MoO_3$
Mo_5O_{12}	=	$3MoO_2, 2MoO_3$
W_2O_5	=	WO_2, WO_3
W_3O_8	=	$WO_2, 2WO_3$
W_4O_{11}	=	$WO_2, 3WO_3$
U_2O_5	=	UO_2, UO_3
U_3O_8	=	$UO_2, 2UO_3$

Compounds corresponding with the Various Oxides

Chromous salts, corresponding with the oxide CrO, are prepared by the reduction of acidified solutions of chromic salts or chromates in absence of air. They are white when anhydrous and blue when hydrated. They oxidize with the greatest ease, forming, when solid, basic chromic salts. A blue solution containing a chromous salt on exposure to air rapidly turns green, by formation of chromic salt. The acetate is the most stable salt; the sulphate, $CrSO_4$, $7H_2O$, is isomorphous with ferrous sulphate, and forms the double salt $CrSO_4$, K_2SO_4, $6H_2O$.

* Collenburg, *Zeitsch. anorg. Chem.*, 1918, **102**, 147.

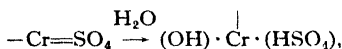
The oxide MoO gives rise to no salts.

The **chromic salts**, corresponding with the oxide Cr_2O_3 and the hydroxide $Cr(OH)_3$, are usually prepared from chromates by reduction:

$$2CrO_3 = Cr_2O_3 + 3O.$$

Thus from potassium dichromate and sulphuric acid, on reduction by alcohol or sulphurous acid, or by nascent hydrogen, as in the bichromate cell, a solution is formed from which the alum K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$ crystallizes.

Chromic sulphate, occurring in violet crystals, has the composition $Cr_2(SO_4)_3$, 18(or 17)H_2O.

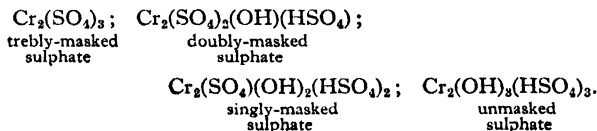
A green salt, having the composition $Cr_2(SO_4)_3$, $6H_2O$, has, however, been obtained by Colson by the action of sulphur dioxide on chromic acid at $-4°$. By the behaviour of this salt when dissolved in water it appears that three forms of it exist. For a freshly prepared solution gives no precipitate with barium chloride; on standing, however, the solution develops sulphate corresponding first with one-third, then with two-thirds, and finally with all the sulphate actually present in the salt. Moreover, as this final stage is reached the solution becomes violet, so revealing the stable colour of chromic salt solution. Colson,* who has investigated these phenomena, speaks of the non-ionized sulphate radicles as "masked sulphate", and attributes the unmasking of sulphate to the incorporation of a molecule of water thus:

$$-Cr{=}SO_4 \xrightarrow{H_2O} (OH)\cdot \overset{|}{Cr}\cdot(HSO_4),$$

and consequently assigns the following formulæ to the four forms of the salt:

$Cr_2(SO_4)_3$; trebly-masked sulphate

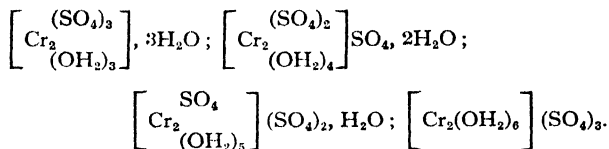
$Cr_2(SO_4)_2(OH)(HSO_4)$; doubly-masked sulphate

$Cr_2(SO_4)(OH)_2(HSO_4)_2$; singly-masked sulphate

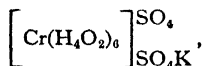
$Cr_2(OH)_3(HSO_4)_3$. unmasked sulphate

* *Bull. Soc. Chim.* (1907), [iv], **1**, 438.

Similar conclusions are expressed by the following formulæ constructed in accordance with Werner's views, since sulphate radicles displaced by water molecules from co-ordinated positions, i.e. from within the square brackets in the formula, thereby become ionizable.

$$\left[Cr_2{}^{(SO_4)_3}_{(OH_2)_3}\right], 3H_2O ; \left[Cr_2{}^{(SO_4)_2}_{(OH_2)_4}\right]SO_4, 2H_2O ;$$

$$\left[Cr_2{}^{SO_4}_{(OH_2)_5}\right](SO_4)_2, H_2O ; \left[Cr_2(OH_2)_6\right](SO_4)_3.$$

These formulæ are interesting for several reasons. First, they account for the water of hydration in $Cr_2(SO_4)_3, 6H_2O$; second, they show in each case six co-ordinated radicles or molecules associated with Cr_2; third, they represent all the water molecules originally present in the crystallized salt as associated with chromium, when the solution has become violet and all its sulphate is ionized; i.e. that a violet solution of a chromic salt contains not $Cr^{\cdots}$ ions but ions of $[Cr_2(OH_2)_6]^{:::}$ or $[Cr(OH_2)_3]^{\cdots}$.

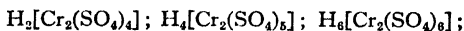
Incidentally it follows that violet chromic sulphate and chromic alum may have a similar constitution in the solid state. Werner represents chromic alum thus:

$$\left[Cr(H_4O_2)_6\right]^{SO_4}_{SO_4K},$$

and so accounts for water of crystallization. It is part of a system of formulating inorganic compounds developed by Werner for metallic ammines (q.v.).

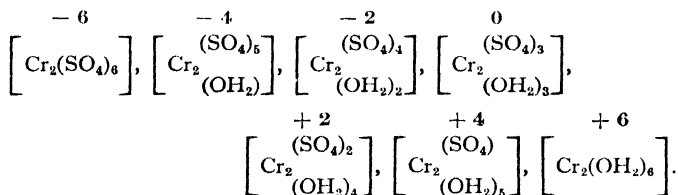
When chromic alum crystals are heated to 90° they lose some water and turn green. The product, which, when dissolved in cold water gives no precipitate with barium chloride, is potassium chromisulphate,* $K_2[Cr_2(SO_4)_4]$, a salt which, disregarding water of crystallization, is isomeric with potassium chromic alum. The following chromisulphuric

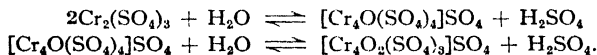
* According to Colson (*Compt. rend.* (1907), 144, 206) a condensed sulphate, $Cr_4(SO_4)_6$, is formed.

acids have been obtained by the combination of chromic sulphate with sulphuric acid:

$$H_2[Cr_2(SO_4)_4]\,;\ H_4[Cr_2(SO_4)_5]\,;\ H_6[Cr_2(SO_4)_6]\,;$$

and it is interesting to observe that, if a sufficiency of water may be assumed within the complex acidic radicles, these acids form the preceding part of a series which is completed by the four varieties of chromic sulphate formulated above. The complete series of complex radicles, with their valencies, thus becomes:

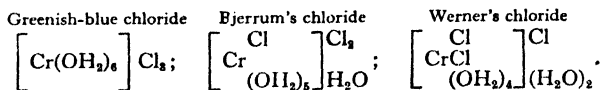
$$\overset{-6}{\left[Cr_2(SO_4)_6\right]},\ \overset{-4}{\left[Cr_2{}^{(SO_4)_5}_{(OH_2)}\right]},\ \overset{-2}{\left[Cr_2{}^{(SO_4)_4}_{(OH_2)_2}\right]},\ \overset{0}{\left[Cr_2{}^{(SO_4)_3}_{(OH_2)_3}\right]},$$

$$\overset{+2}{\left[Cr_2{}^{(SO_4)_2}_{(OH_2)_4}\right]},\ \overset{+4}{\left[Cr_2{}^{(SO_4)}_{(OH_2)_5}\right]},\ \overset{+6}{\left[Cr_2(OH_2)_6\right]}.$$

A further fact to be recorded is that when chromic sulphate solution is boiled it turns green and becomes acid. From the green solution only one-third of the sulphate can be precipitated by barium chloride; and since hydrolysis takes place the following reactions are believed to occur with the formation of condensed chromic sulphates: *

$$2Cr_2(SO_4)_3 + H_2O \rightleftharpoons [Cr_4O(SO_4)_4]SO_4 + H_2SO_4$$
$$[Cr_4O(SO_4)_4]SO_4 + H_2O \rightleftharpoons [Cr_4O_2(SO_4)_3]SO_4 + H_2SO_4.$$

Chromic chloride, $CrCl_3$, when prepared in the dry way, consists of pink scales which are insoluble in water and chemically inert. In the solid hydrated condition as $CrCl_3, 6H_2O$, chromic chloride exists in one greenish-blue and two green forms.† The greenish-blue salt dissolves in cold water, forming a bluish-violet solution from which silver nitrate precipitates all the chlorine in the salt; both green chlorides form green solutions, from one of which silver nitrate preci-

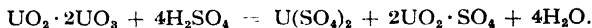
* Colson, *loc. cit.*
† Gubser and Werner, *Ber.* (1901), **34**, 1601; Bjerrum, *Ber.* (1906), **39**, 1599.

pitates two-thirds of the chlorine present, and from the other only one-third. These latter salts are known respectively as Bjerrum's and Werner's chloride, and the constitutions of the three salts are thus represented by Werner:

Greenish-blue chloride	Bjerrum's chloride	Werner's chloride
$\left[Cr(OH_2)_6\right]Cl_3$;	$\left[Cr\begin{matrix}Cl\\ (OH_2)_5\end{matrix}\right]\begin{matrix}Cl_2\\ H_2O\end{matrix}$;	$\left[CrCl\begin{matrix}Cl\\ (OH_2)_4\end{matrix}\right]\begin{matrix}Cl\\ (H_2O)_2\end{matrix}$.

This is an example of what is called "Hydrate Isomerism". Both green salts when in solution revert gradually to the fully ionized salt.

Chromic sulphide, like aluminium sulphide, can be formed only in the dry way, and is hydrolyzed by water.

Of salts corresponding with the **oxides MO_2**, those of uranium, the **uranous salts**, are the only ones to be considered. These salts, which are obtained in solution by the reduction of an acidified uranyl solution with zinc, are green, and yield green crystals; e.g. UCl_4 and $U(SO_4)_2, 9H_2O$. The sulphate also results, together with uranyl sulphate, when pitchblende, U_3O_8, is acted on by sulphuric acid,

$$UO_2 \cdot 2UO_3 + 4H_2SO_4 = U(SO_4)_2 + 2UO_2 \cdot SO_4 + 4H_2O.$$

Like the chromous salts, the uranous salts are powerful reducing agents, reducing ferric to ferrous salts, and precipitating gold and silver from their salt solutions.

As previously mentioned, the **oxides MO_3** are chiefly acidic; MoO_3 exhibits feebly, and UO_3 more powerfully basic properties. The acids, with the probable exception of chromic acid, cannot be obtained in a pure state by combination of the oxides with water. CrO_3 is a red crystalline substance easily soluble in water, the solution containing dichromic acid,* $H_2Cr_2O_7$. MoO_3 is a white powder, slightly soluble in water, yielding a solution which reacts acid; WO_3 (canary yellow) and UO_3 (orange or red) are insoluble in water, but WO_3 is soluble in boiling aqueous alkalis.

* Pellini, *Gazzetta* (1916), **46**, ii, 247.

Acids derived from MO_3, and their Salts

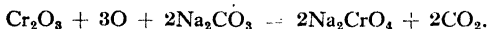
Acids of the type H_2MO_4 are known in the case of each of these four elements.

Chromic acid, H_2CrO_4, crystallizes in rose-red crystals from the solution obtained by digesting CrO_3 with less than sufficient water to dissolve it. The acid separates into CrO_3 and water on warming.

So little tendency does CrO_3 show to combine with a molecule of water to form H_2CrO_4, that the anhydride itself crystallizes from a chromate solution to which concentrated sulphuric acid is added. Since $H_2Cr_2O_7$ exists in an acidified chromate solution, the anhydride may be supposed to be the final dehydration product of the action of concentrated sulphuric acid on dichromic acid.

Molybdic acid, H_2MoO_4, is a white, crystalline powder obtained when a nitric-acid solution of MoO_3 evaporates spontaneously. The hydrate, H_2MoO_4, H_2O, crystallizes in yellow crusts from a nitric-acid solution of ammonium molybdate. **Tungstic acid,** H_2WO_4, is a yellow powder insoluble in water and most acids. H_2WO_4, H_2O, soluble in water, is obtained by precipitating a tungstate by acid in the cold. Hydrated **uranic acid,** H_2UO_4, H_2O, is obtained as a yellow mass by evaporating a solution of uranyl nitrate, $UO_2(NO_3)_2$, in alcohol.

Salts of the type R_2MO_4 are known for all four elements; only the **chromates** are important. The alkali chromates are lemon-yellow, and are obtained by the action of alkalis and oxidizing agents on chromic oxide; thus:

$$Cr_2O_3 + 3O + 2Na_2CO_3 = 2Na_2CrO_4 + 2CO_2.$$

When a chromate is prepared by fusion, the oxygen may be supplied either from potassium chlorate or nitrate, or from the atmosphere. In the wet way precipitated chromic hydroxide may be oxidized by alkaline hydrogen peroxide, produced from sodium peroxide, by hypochlorites, or by lead peroxide.

Condensed or poly-acids and their salts.—It was observed in the case of sulphuric acid and its salts that condensation of two molecules may take place under certain conditions to form disulphates. A similar phenomenon is noticed with other oxyacids, such as phosphoric, iodic, and boric, but is unknown with nitric acid. It is specially characteristic of the weak oxyacids of Group VI A, so that indeed the more complex acids and their salts are for the most part obtained more readily than the simple ones.

When normal chromates are treated with acids, **dichromates** are formed, thus:

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + H_2O.$$

Potassium dichromate, in turn, yields, with chromic anhydride, or on boiling with moderately concentrated nitric acid, the **trichromate** $K_2Cr_3O_{10}$; and this, again, with concentrated nitric acid, gives the **tetrachromate** $K_2Cr_4O_{13}$.

These salts may be represented thus (though oxygen is really tetrahedrally disposed round chromium):

$$CrO_2\begin{matrix}\diagup OK\\ \diagdown OK\end{matrix}$$

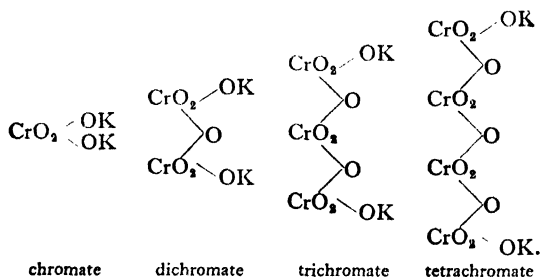
chromate

$$\begin{matrix}CrO_2 - OK\\ \quad >O\\ CrO_2 - OK\end{matrix}$$

dichromate

$$\begin{matrix}CrO_2 - OK\\ \quad >O\\ CrO_2\\ \quad >O\\ CrO_2 - OK\end{matrix}$$

trichromate

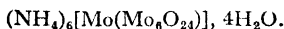
$$\begin{matrix}CrO_2 - OK\\ \quad >O\\ CrO_2\\ \quad >O\\ CrO_2\\ \quad >O\\ CrO_2 - OK.\end{matrix}$$

tetrachromate

Water hydrolyzes tri- and tetrachromates to dichromates and chromic acid, and excess of alkali reconverts all the condensed chromates to the normal salts.

Molybdic and tungstic acids are more, and uranic acid is less, prone to condensation than chromic acid.

The general formula for **condensed or poly-molybdates** may be written $R'_2O, xMoO_3$, where $x = 1, 2, 3, 4, 7, 8,$ or 10

Tri-molybdates are common. There are also salts derived from condensation of the next hydrated acid, H_4MoO_5; ordinary ammonium molybdate or paramolybdate, for instance, is $(NH_4)_6Mo_7O_{24}, 4H_2O$; its constitution probably being

$$(NH_4)_6[Mo(Mo_6O_{24})], 4H_2O.$$

The polytungstates are even more complex than the polymolybdates. Tetratungstic acid, $H_2W_4O_{13}, 7H_2O$, is a crystalline substance soluble in water. Commercial sodium tungstate possesses the composition $Na_{10}W_{12}O_{41}, 28H_2O(Na_{10}W_{12}O_{41} = 5Na_2O, 12WO_3)$.

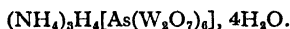
In addition to the above method of condensation, molybdic and tungstic acids likewise possess the power of combining with phosphoric and other acids of a similar type to form:

Heteropoly acids. These acids conform to the type * $H_{12-n}[R^n(M_2O_7)_6]$, where R is an element of valency *n*, such as B, Si, P, As, Ti, Ge, Zr, Sn, H_2, and M is molybdenum or tungsten; and since there are 12 atoms of either of the two latter elements within the acidic complex, the acids are called **12-acids.** They generally crystallize with 28 or 22 molecules of water.

The following acids of this type are known, the composition of which may be made clearer by showing also the component oxides, thus:

12-borotungstic acid,† $H_9[B(W_2O_7)_6]$ or $9H_2O, B_2O_3, 24WO_3$.
12-silicomolybdic acid, $H_8[Si(Mo_2O_7)_6]$ or $4H_2O, SiO_2, 12MoO_3$.
12-silicotungstic acid, $H_8[Si(W_2O_7)_6]$ or $4H_2O, SiO_2, 12WO_3$.
12-phosphomolybdic acid, $H_7[P(Mo_2O_7)_6]$ or $7H_2O, P_2O_5, 24MoO_3$.
12-phosphotungstic acid, $H_7[P(W_2O_7)_6]$ or $7H_2O, P_2O_5, 24WO_3$.
12-arsenotungstic acid, $H_7[As(W_2O_7)_6]$ or $7H_2O, As_2O_5, 24WO_3$.

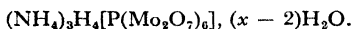
This last acid is not known, but its ammonium salt is:

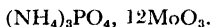
$$(NH_4)_3H_4[As(W_2O_7)_6], 4H_2O.$$

To ammonium phosphomolybdate, the precipitate ordinarily

* Rosenheim and Jänicke, *Zeitsch. anorg. Chem.* (1917), **101**, 235.

† Sometimes an alternative nomenclature, e.g. tungstoboric, molybdophosphoric, acid, is employed.

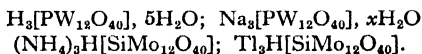
obtained in testing for phosphate, the formula $(NH_4)_3PO_4$, $12MoO_3$, xH_2O is attributed. This salt is apparently analogous to the above ammonium arsenotungstate, and therefore may be represented thus:

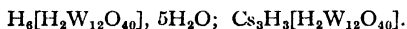
$$(NH_4)_3H_4[P(Mo_2O_7)_6], (x - 2)H_2O.$$

When dried above 130° the salt becomes anhydrous, and is then

$$(NH_4)_3PO_4, 12MoO_3.$$

Chromium forms few of such compounds, and uranium none.

The crystal structures of lower hydrates of the above acids and their salts indicate (Illingworth and Keggin, 1935) that the acids conform to the type $H_{8-n}[R^nW_{12}O_{40}]$, thus possessing a lower basicity than shown above.

Some of the compounds examined are thus:

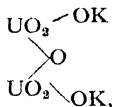
$$H_3[PW_{12}O_{40}], 5H_2O; \quad Na_3[PW_{12}O_{40}], xH_2O$$
$$(NH_4)_3H[SiMo_{12}O_{40}]; \quad Tl_3H[SiMo_{12}O_{40}].$$

Meta-tungstic acid is a 12-acid, thus:

$$H_6[H_2W_{12}O_{40}], 5H_2O; \quad Cs_3H_3[H_2W_{12}O_{40}].$$

These formulæ depend on the X-ray analysis of 5-hydrated phosphotungstic acid by Keggin (1934), which revealed that the element R is surrounded tetrahedrally by four oxygen atoms. Beyond this is a shell of twelve tungsten atoms, each one surrounded octahedrally by six oxygen atoms. Sharing of oxygen occurs, and every three octahedra possess one of the tetrahedral oxygen atoms in common. The charge on the anion is neutralized by the positive cations. Water of crystallization is inserted interstitially, the fully hydrated acid being the 29-hydrate. These structures agree with the lower basicity generally shown in alkali salts, and the co-ordination number, 4, for R is normal.

Rosenheim's formulæ, on the other hand, endow R with a co-ordination number of 6, and in agreement therewith, the higher basicity appears in a few mercurous and guanidinium salts, e.g.:

$$Hg_8[Si(W_2O_7)_6], 5H_2O; \quad (CH_5N_3{\cdot}H)_7[P(W_2O_7)_6], 12H_2O.$$

The chief **uranates** are derived from the acid $H_2U_2O_7$. When potassium hydroxide is added to uranyl nitrate solution, $UO_2(NO_3)_2$, the yellow precipitate obtained consists of uranyl hydroxide together with some potassium diuranate,

$$\begin{array}{l} UO_2\diagup OK \\ \quad \rangle O \\ UO_2\diagdown OK, \end{array}$$

which is thus insoluble in water. The sodium salt, $Na_2U_2O_7$, $6H_2O$, is uranium yellow; glass coloured with this substance is bright yellow, and shows a green fluorescence. Tri- and tetra- as well as monouranates are known.

Reference has previously been made to **uranyl salts.** The existence of these salts is due to the fact that uranium trioxide, alone among trioxides, possesses distinctly basic properties. This is due to the superior metallic character of uranium, a fact indicated by its high atomic weight and position as the last member of Group VI A of the periodic table. One only of the three oxygen atoms can, however, be replaced by acid radicles; and thus basic salts, known as the uranyl salts, result.

The **nitrate,** $UO_2(NO_3)_2$, $6H_2O$, is the best-known salt. It is yellow and possesses a green fluorescence. Certain organic salts, such as the oxalate, are sensitive to light, being thus reducible to uranous compounds. Uranyl ammonium phosphate, $UO_2NH_4PO_4$, is a greenish-yellow precipitate, insoluble in acetic acid; it is obtained in a process for the volumetric estimation of phosphates. The ferrocyanide forms a brown precipitate.

Chromium forms series of complex cyanides and ammines, which will be dealt with under Group VIII.

CHAPTER XI

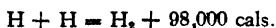
HYDROGEN

Hydrogen	H^1	1·0081.
Deuterium	H^2 or D	2·0148.
Tritium	H^3 or T	3·0151.

In the modern periodic system, hydrogen shares with helium the first short period, but may be regarded as showing affinities with both lithium and fluorine. Hydrogen gas is liquefied at −252·5° C. under 760 mm. pressure: the white ice-like solid, M.P. −258·4° C., finally discredited the idea that hydrogen was a metal of low melting-point.

Constituted of one proton and one electron, hydrogen may exercise electronegative character and gain one more electron, either electrovalently, as in $Li[H]^-$, or covalently, as in anhydrous HCl. This latter, however, ionizes and dissociates in ionizing solvents to form H^+, thus displaying the electro-positive character which places hydrogen among the metals in the electro-chemical series. Mono-electronic hydrogen links are assumed in the boron hydrides, and the hydrogen bond occurs with an electronegative atom, as in hydrate formation, =O···H—O—H.

Atomic hydrogen.—For long, "nascent" or atomic hydrogen was assumed to account for the strong reducing properties shown when the gas is generated *in situ*; there is evidence that this is correct (H. S. Taylor, 1926). Atomic hydrogen is obtained when molecular hydrogen is dissociated by hot filaments of tungsten, palladium, or platinum, the gas being at low pressure, 0·01–0·001 mm. (Langmuir, 1915). It is also formed by the action of ultra-violet light on hydrogen. This form is very active, uniting readily with S, P, As, Ge, Sn, but not with nitrogen, to give the hydrides. The free atom is short-lived, recombination occurring, thus:

$$H + H = H_2 + 98{,}000 \text{ cals.}$$

By blowing hydrogen through an electric arc, atomic

hydrogen is formed, which, by recombination in the sense of the above equation, produces a temperature sufficiently high to melt tungsten (M.P. 3660°).

Hydrogen gas dissolves in platinum and palladium, presumably in the atomic state, and diffuses therefrom in the same state, manifesting its activity by combining, for example, with oxygen at room temperature, and with phosphorus to form phosphine.

Triatomic hydrogen, H_3 (hyzone, on analogy with ozone) was first detected as H_3^+ by Sir J. J. Thomson in positive ray analysis. The reported occurrence of H_3 in other reactions is not confirmed.

Ortho- and para-hydrogen.—The occurrence of helium in two similar forms was explained by Heisenberg (1926) on the basis of quantum mechanics, and the prediction was made that hydrogen should show similar allotropes. These arise because the protons in the H_2 molecule possess "spins" which, in the ortho-form are parallel, and in the para-form, are anti-parallel. The two forms of the helium atom are due to the relative spins of its two electrons. The bonding electrons of H_2, however, have anti-parallel orientation, otherwise union would not occur. Ordinary hydrogen is an equilibrium mixture containing 25 per cent para-form. If the gas be adsorbed on charcoal at 20° Abs., the catalytic conversion to the para-form is practically complete. The two forms differ in physical properties. Para-hydrogen is stable at ordinary temperature, but reversion to the equilibrium mixture is caused by catalysts, by paramagnetic molecules, e.g. NO_2 and O_2, and by atomic hydrogen.

Heavy hydrogen, deuterium (or diplogen), D or H^2.

By the mass spectrograph, Aston found the mass of the hydrogen atom to be 1·00778, measured against the oxygen atom, $O^{16} = 16$.

The average chemical atomic weight, measured against oxygen in bulk, was 1·00777. This excellent agreement was upset by the discovery that natural oxygen contains the

isotopes, O^{16}, O^{17}, O^{18}, and, from their relative abundance, it was estimated that this oxygen should give, when compared with the physical standard, $O^{16} = 16$, an atomic weight, not of 16, but of 16·0035, that is, 1·00022 times higher; whence it follows that the chemical value for hydrogen on the physical scale, should be

$$1{\cdot}00777 \times 1{\cdot}00022 = 1{\cdot}00799$$

a discrepancy of 2 in 10,000. Birge and Menzel (1931) concluded that this was greater than the experimental error, and suggested that ordinary hydrogen contained a heavier isotope. By fractionation of liquid hydrogen, Urey, Brickwedde and Murphy (1932) demonstrated its presence spectroscopically.

The mass of the new isotope D, is 2·0148, and it is present in hydrogen from rain water to the extent of 1 in 5000 (approx.). This concentration can be increased by distilling liquid hydrogen, by diffusion methods or adsorption on charcoal. The isotope is present in water as D_2O or DHO; a separation from H_2O occurs when the mixture is passed over hot iron, or when the acidified water is treated with zinc, or when alkaline water is electrolyzed. In all three processes, preferential decomposition of H_2O occurs, the residue being enriched with D_2O. The electrolytic method is the main source of D_2O and heavy hydrogen.

Some constants for the two types of hydrogen and water are given here:

	B.P.	M.P.	Sp. Gr. at 20°	Temp. of max. dens.
H_2	20·38° Abs.	13·95° Abs.		
D_2	23·5° Abs.	18·59° Abs.		
H_2O	100° C.	0° C.	0·9982	4° C.
D_2O	101·4° C.	3·82° C.	1·1059	11·6° C.

The ratio of the two isotopes present in the gaseous mixture may be determined by the spectroscope, by the mass spectrograph, by thermal conductivity methods, or the gas may be converted to water whose specific gravity may be determined.

Hitherto, isotopes of the same atomic number have been

considered to possess identical chemical properties; the two isotopes, H and D, show different chemical activity. The percentage mass difference, which is small in other cases, is here large, hence the molecular velocity of D_2 is the smaller. Moreover, energy considerations are involved, e.g. the minimum amount of energy required for fruitful molecular collisions is higher for D_2 than for H_2. In general, deuterium is less reactive. Thus, with chlorine, DCl is formed at one-third the rate of HCl, whilst the muta-rotation of glucose is faster with H^+ than with D^+, though the opposite holds for the inversion of cane sugar.

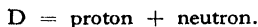
Interesting reactions occur when D interchanges with H, as happens catalytically with water:

$$HD + H_2O \rightleftharpoons HDO + H_2.$$

A similar interchange occurs rapidly with H_2O_2 and D_2O. In alkaline D_2O, all six H atoms of acetone are rapidly replaced. Glucose interchanges only the hydroxyl hydrogen, while benzene is inert in the absence of catalysts. New compounds containing deuterium thus arise, e.g. DCN, CH_3COOD (deutacetic acid). By the reaction of Mg_3N_2 with D_2O there results deuteroammonia, ND_3, M.P. $-74°$ C. (NH_3 melts at $-77{\cdot}8°$ C.).

The importance of deuterium is obvious; it is useful in syntheses, as a hydrogen " indicator " in reactions (as O^{18} is for oxygen), in kinetic studies, and lastly, the deuteron, D^+, is used as a heavy projectile to effect nuclear transformations.

By means of γ-rays, Chadwick (1934) has succeeded in breaking up the deuterium nucleus thus:

$$D = \text{proton} + \text{neutron}.$$

Tritium. There are indications that a third isotope exists, $H^3 = 3{\cdot}1015$. It is present in ordinary water to the extent of 7 parts in 10^{10}. This must not be confused with H_3, hyzone.

GROUP VII

Sub-group A		Sub-group B
	9 F (19·0)	
	17 Cl (35·46)	
25 Mn (54·93)		35 Br (79·92)
43 Ma		53 I (126·92)
75 Re (188·7)		——

THE HALOGEN ELEMENTS

Fluorine, Chlorine, Bromine, and Iodine

Of the six best-known members of the seventh group, the four halogen elements, fluorine, chlorine, bromine, and iodine, form a family of closely allied elements; whilst manganese and rhenium are in most respects quite dissimilar from them.

Fluorine is the most electro-negative of all the elements, and the characteristics of the halogens as a class are almost entirely electro-negative in accordance with the positions they occupy as terminal members of the various periods.

There is an increase of electro-positiveness from fluorine through chlorine and bromine to iodine, and a corresponding decrease in chemical activity towards hydrogen and all elements which manifest any electro-positive properties.

The extraordinary affinity of fluorine for hydrogen, which is manifested by its power of combining with this element in the dark, and displacing chlorine from hydrogen chloride, has been supposed to be accompanied by complete inability to combine with oxygen. Nevertheless it has been shown * that a gaseous oxide of fluorine, probably F_2O, is formed in the electrolysis of molten acid potassium fluoride below 100° in the presence of water. The gas has been obtained, not pure but mixed with oxygen; and such a mixture has the odour of fluorine, is soluble in alkali and liberates iodine from potassium

* Lebeau and Damiens, *Compt. rend.* (1927), **185**, 652.

iodide, but is stable in the presence of water, in which it is only sparingly soluble. The oxides, F_2O_2 and FO also exist.

A notable characteristic of fluorine is the formation of polyfluorides such as SF_6, SeF_6, TeF_6, OsF_8, when the corresponding chlorides do not exist. In these fluorides the elements forming them employ their highest valencies, and since the compounds are gaseous, or at least volatile, though they show no tendency to dissociate, the fluorine atoms within them must be intimately linked with the nuclear atoms, and neutralize them, so that there is no superfluous field of attraction to promote association and cause non-volatility.

Nitrogen forms a stable fluoride, NF_3, whilst fluorides of the other elements of the fifth group are well known. Fluorine forms with other halogens the compounds:

$$ClF, BrF; ClF_3, BrF_3; BrF_5, IF_5; IF_7.$$

It does not unite directly with gold or platinum, although these metals are attacked by chlorine.

The stability of the compounds which the halogens form with oxygen increases from chlorine to iodine, though in some at least of its reactions bromine shows less affinity for oxygen than chlorine. Thus the superior affinity of iodine for oxygen is shown by the fact that it displaces chlorine from potassium chlorate according to the reaction

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2,$$

and also by the direct oxidation of iodine to iodic acid by means of nitric acid. This increase in stability of oxygen compounds, with rising atomic weight, is the opposite of what obtains in Group VI B.

With reference to other inter-halogen compounds it may be remarked that with bromine the monochloride, BrCl, is known, and iodine gives ICl, ICl_3, and IBr. For the most part, inter-halogen compounds are formed by direct union. It will be observed that the power possessed by the halogens

of forming compounds with one another depends upon the electro-chemical difference between the atoms forming the compounds.

Preparation of the Halogens

The following methods are available:

(i) Oxidation of the hydracid in aqueous solution.

(ii) Electrolysis of halides under favourable conditions, secondary reactions being guarded against.

(iii) The decomposition of a perhalide by heat, just as oxygen is obtained by the decomposition of manganese or lead peroxide.

(iv) Displacement of one halogen by another.

(i) The oxidation of a hydracid according to the reaction

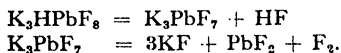
$$2HX + O = H_2O + X_2$$

depends essentially upon the looseness of attachment of the halogen element to hydrogen. Now, since fluorine combines with hydrogen in the dark, and decomposes water instantly, it is not to be expected that this element will be obtained by the above reaction. The other halogens, however, in accordance with their decrease in electro-negativeness from chlorine to iodine, may be prepared by the use of oxidizing agents with increasing ease. If a mixture of air or oxygen with the moist hydracid is passed through a heated tube, no change takes place in the case of hydrofluoric acid, partial oxidation with hydrochloric acid, and more rapid and complete action with hydrobromic and hydriodic acids. When the moist hydracids are mixed with oxygen and exposed to sunlight the reaction extends from zero with hydrofluoric to a maximum with hydriodic acid, the same being true of solutions of the acids in water. This gradation of oxidizability is further illustrated by the fact that sulphuric acid, which does not oxidize hydrogen chloride, liberates bromine and iodine from their hydracids when they are being prepared by warming that acid with bromides and

iodides respectively. The possibility of the reverse action, in which the free element decomposes water, diminishes rapidly on passing from fluorine to the other halogens. Upon this diminution depends the loss of bleaching power on passing from chlorine to bromine and iodine.

(ii) Whilst chlorine, as well as bromine and iodine, can be obtained by the electrolysis of aqueous solutions of the corresponding alkali halides, it is obvious that fluorine cannot be obtained by this method in the presence of water. The means by which Moissan, in 1886, obtained fluorine consisted in the application of this powerful method of decomposition to a solution of potassium fluoride in anhydrous hydrofluoric acid, such a solution being an anhydrous electrolyte.

(iii) The applicability of the third method depends upon the existence of polyhalides of certain elements which are more stable at low than at high temperatures. Considering fluorine, for instance, and the compounds it forms with elements from the first group onwards: whilst the mono-, di-, and trifluorides of the first three groups respectively will not undergo such decomposition, in the fourth group a condition is reached in which the atoms of certain elements, whilst forming tetrafluorides, do not manifest sufficient affinity for fluorine to retain four atoms in combination at high temperatures. Thus cerium tetrafluoride was found by Brauner, in 1882, to break up, when heated, into fluorine and a lower fluoride. Fluorine was also obtained later by the same chemist by the action of heat on potassium hydrogen fluorplumbate,

$$K_3HPbF_8 = K_3PbF_7 + HF$$
$$K_3PbF_7 = 3KF + PbF_2 + F_2.$$

In the same way $PbCl_4$ easily breaks up into $PbCl_2$ and Cl_2, and in the familiar process for the preparation of chlorine from manganese dioxide and hydrochloric acid, manganic chloride, $MnCl_3$, is formed as an intermediate product which breaks up into manganous chloride and chlorine when heated.

(iv) Each halogen will displace from combination those

which follow it in the group. Chlorine is thus used to displace bromine or iodine in analysis and chemical manufacture.

An examination of the physical properties of the halogen elements, as given in the table on the following page, shows a regular gradation from fluorine to iodine. This is manifested in the rise of melting- and boiling-points, and in deepening colour; the densities of the liquid elements likewise increase in the same order. Solubility in water, however, diminishes from chlorine to iodine. Power of dissociation of the di-atomic molecules into atoms by heat increases from fluorine to iodine. No dissociation has been observed in the case of fluorine gas; chlorine manifests a sensible diminution in density above 1450°; the density of bromine vapour becomes two-thirds of its normal value at 1570°; whilst in the case of iodine the density of the vapour begins to diminish at 700° and becomes half its normal value at 1700°, above which temperature the element exists in the atomic state.

This increase in readiness to dissociate with rise of atomic weight and increase in electro-positiveness, is consistent with an approximation to the character of metallic vapours, which, so far as observation goes, appear to exist in a monatomic state.

Relationships between the chemical characters of these elements appear in the study of their compounds. More chemical differences will be observed between fluorine and chlorine than between the other successive members of the group; it has previously been seen that the properties of the first member of a group are somewhat exceptional. Chlorine, bromine, and iodine, indeed, form a triad of elements, the atomic weight of bromine standing midway between those of chlorine and iodine. Fluorine stands outside this triad by reason of many of its properties. This is illustrated in the following table of atomic numbers and weights and their differences:

	At. Numbers.	Differences.	At. Weights.	Differences.
F	9		19·0	
		8		16·46
Cl	17		35·46	
		18		44·46
Br	35		79·92	
		18		47·00
I	53		126·92	

SUMMARY OF GROUP VII

Properties of Element.	F	Cl	Br	I	Mn
Atomic weight	19·0	35·46	79·92	126·92	54·93
Appearance	pale greenish-yellow gas	greenish-yellow gas	deep reddish-brown liquid	violet-black solid with metallic lustre	lustrous metal
Melting-point	−233°	−102°	−7·3°	114°	1245°
Boiling-point at atm. pressure	−187°	−33·6°	58–59°	184°	—
Density of liquid	1·14 (at B.P.)	1·556 (at B.P.)	2·982 (at B.P.)	—	—
Density of solid	—	> 1·66 (at M.P.)	—	4·95	7·4
Types of compounds.					
Hydrides HX	$HF(H_2F_2)$	HCl	HBr	HI	—
Oxides and hydroxides—					
X_2O	F_2O	Cl_2O	Br_2O	—	—
XOH	—	*ClOH	*BrOH	*IOH	—
XO	F_2O_2; FO	—	—	—	MnO (basic)
X_3O_4	—	—	—	—	Mn_3O_4 (neutral)
X_2O_3	—	—	—	—	Mn_2O_3 (basic)
$XOOH$	—	*ClOOH	—	—	MnOOH (basic)
XOR	—	—	—	IOC_6H_5 (basic oxide)	—
XO_2	—	ClO_2 (mixed anhydride)	BrO_2	IO_2	MnO_2 (functions various)
X_2O_5	—	—	—	I_2O_5	—
XO_2OH	—	*ClO_2OH	*BrO_2OH	IO_2OH	—
XO_2R	—	—	—	$IO_2C_6H_5$ (basic peroxide)	—
XO_3	—	Cl_2O_6	—	—	MnO_3 (acidic)
$XO_2(OH)_2$	—	—	—	—	$MnO_2(OK)_2$
X_2O_7	—	Cl_2O_7	—	I_2O_7 (?)	Mn_2O_7 (acidic)
XO_3OH	—	ClO_3OH	—	IO_3OH (and other forms)	MnO_3OH
R_2XOH	—	—	—	R_2IOH (iodonium)	—

* Known only in aqueous solution.

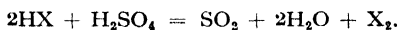
Halogen Hydracids and their Salts

Of the hydracids of the four halogen elements hydrofluoric acid is the most and hydriodic acid the least stable. The heats of formation of these four compounds from their elements are:

HF	386K
HCl	220K
HBr	84K
HI	-60K

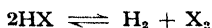
These figures represent the relative stabilities of the four acids. Fluorine will therefore displace chlorine, bromine, and iodine from their compounds with hydrogen or metals, chlorine will displace bromine and iodine, and bromine will displace iodine only.

Reference has already been made to the fact that hydrobromic and hydriodic acids cannot be obtained pure by the action of concentrated sulphuric acid upon the corresponding alkali salts. Bromine and iodine respectively are liberated owing to the oxidation of the hydracids by sulphuric acid in the following way:

$$2HX + H_2SO_4 = SO_2 + 2H_2O + X_2.$$

This is quite in accord with what has just been learned regarding the instability of these acids.

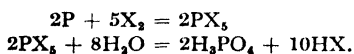
These reactions are reversible, however, hydrobromic and hydriodic acids being produced by interaction of halogen and sulphurous acid in dilute solution.

Hydrogen bromide, and more especially hydrogen iodide, are therefore reducing agents, because of the ease with which they separate into their elements at moderate temperatures. A consideration of the reversible reaction

$$2HX \rightleftharpoons H_2 + X_2$$

shows that the reaction from left to right, which is almost if not quite non-existent in the case of fluorine, increases in ease regularly through chlorine and bromine to iodine. Such dis-

sociation, which constitutes an ordinary reversible reaction in the absence of an oxidizing agent, is, however, promoted by sulphuric acid and other substances which have the power of removing hydrogen from the hydracid, oxidizing it to water.

This decomposition of hydrobromic and hydriodic acids is avoided by substituting phosphoric for sulphuric acid in their preparation, or by the method in which the element is made to react with red phosphorus and water:

$$2P + 5X_2 = 2PX_5$$
$$2PX_5 + 8H_2O = 2H_3PO_4 + 10HX.$$

Whilst hydrogen fluoride resembles hydrogen chloride in its manner of preparation and some of its properties, it differs from the latter, and from the other halogen acids, both in its physical properties and in the nature of the salts which it forms. Hydrogen fluoride boils at 19·4° under atmospheric pressure, whilst the boiling-points of hydrogen chloride, bromide, and iodide are respectively —83·1°, —67·1°, and —35·5°.

This difference is to be explained by the fact that the molecules of hydrogen fluoride exhibit a tendency towards polymerization, so that the molecular weight of this compound is found to be even greater than that of hydrogen chloride under similar circumstances. It has been found, moreover, that the vapour-density of hydrogen fluoride gas varies from 25·6 at 26·4° to 10·3 at 88°, so that the gas consists of H_2F_2 and even larger molecules. It is not surprising, therefore, that acid salts such as KHF_2 exist, and that they are broken up by heat. Fluorine has been regarded as trivalent in these compounds; but a more recent view is that one hydrogen atom becomes bivalent, and links the two fluorine atoms forming the univalent anion: [FHF]. A difference between hydrofluoric and the other hydracids is also illustrated by the existence of such compounds as H_2SiF_6 and HBF_4.

It must further be observed that the fluorides of certain metals differ from the corresponding chlorides, bromides, and iodides. Calcium fluoride, for instance, is insoluble in water, whilst the chloride, bromide, and iodide of this metal are soluble; and, on the other hand, silver fluoride is a soluble, deliquescent salt in contradistinction to the other halides of silver, which are insoluble in water. Mercuric fluoride, too, differs from the chloride, bromide, and iodide in being completely hydrolyzed by water, thus resembling the oxysalts of this metal.

The solubilities of the hydracids in water are as follows, the figures representing the weight of acid which dissolves in 1 gramme of water at 10° C.:

HF	3·32 (at 0° C.)
HCl	0·77
HBr	2·10
HI	2·48.

Again it is seen that hydrofluoric acid is exceptional, its greater solubility being probably connected with its greater condensibility.

Lastly, the relative strengths of the halogen hydracids must be considered.

The following table gives the heats of neutralization and the avidities as determined by Thomsen:

	Heat of Neutralization	"Avidity"
HF	163 K	0·05
HCl	137 K	1·00
HBr	138 K	0·89
HI	137 K	0·70

The degree of electrolytic dissociation of these acids at different states of dilution is given by the following table (Ostwald):

Dilution	HF	HCl	HBr	HI
10 litres	0·10	0·95	0·95	0·95
100 litres	0·26	0·98	0·98	0·98
1000 litres ..	0·59	0·99	0·99	0·99

Since the strength of an acid is indicated by the degree of its electrolytic dissociation at a given dilution, it is manifest that whilst HCl, HBr, and HI are strong acids of about equal strength, HF is a much weaker acid. The values for avidity obtained by Thomsen indicate the same fact. Thus hydrofluoric acid is largely displaced from sodium fluoride by the stronger hydrochloric acid. It is important, therefore, to recognize that the relative strengths of these acids are not in the order of the electro-negativeness of the halogen elements which they contain, or of their relative stability. The weakness of hydrofluoric acid is at first sight surprising, since it would be thought that such an extremely active and electronegative element as fluorine must needs produce a powerful acid. Now if an atom of fluorine were a constituent of the molecule of an oxyacid, it would no doubt by its presence promote the separation of hydrogen ions just as chlorine does in the chloracetic acids, the strength of the acid thus being increased by substitution. In the case of hydrofluoric acid, however, the fluorine atom is united directly to the hydrogen atom of the acid; and, moreover, the acid is exceptional in forming molecules of H_2F_2 which constitute the imperfectly ionized monobasic acid H[FHF].

The excess of heat of neutralization of hydrofluoric acid over 137K (viz. 26K) is the heat evolved by the acid in reaching a state of complete ionization in solution during the process of neutralization.

Oxides and Oxyacids of Chlorine, Bromine, and Iodine

The following are the types of oxyacids formed by these elements:

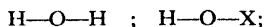
HOX, e.g. hypochlorous acid HOCl
HOXO, e.g. chlorous acid HOClO or $HClO_2$
$HOXO_2$, e.g. chloric acid $HOClO_2$ or $HClO_3$
$HOXO_3$, e.g. perchloric acid $HOClO_3$ or $HClO_4$.

Only in the case of chlorine is the series complete; bromous

acid possibly exists, but not perbromic acid, $HBrO_4$; iodous acid, HIO_2, is unknown.

Of the anhydrides corresponding with these acids, namely X_2O, X_2O_3, X_2O_5, and X_2O_7 respectively, chlorine forms Cl_2O and Cl_2O_7, iodine I_2O_5, and possibly I_2O_7, whilst bromine forms Br_2O. Other oxides known are, ClO_2, Cl_2O_6, ClO_4; BrO_2, $(Br_3O_8)_n$; IO_2, I_4O_9 and IO_4.

Acids of the type HOX are weak and unstable. On account of their feebly acidic character they may be represented as derivatives of water,* in which one hydrogen atom is replaced by halogen thus:

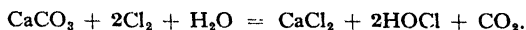
$$H—O—H \quad ; \quad H—O—X;$$

and indeed halogen can displace hydrogen from water itself to some extent according to the reaction,

$$HOH + X_2 \rightleftharpoons HOX + HX;$$

and if cold dilute alkali is employed, so that the acids produced are neutralized, the change is completed according to the equation

$$2KOH + X_2 = KOX + KX + H_2O.$$

The weakness of these acids is further shown by the fact that they are completely displaced from combination by such weak acids as carbonic and acetic acids. If, accordingly, chlorine gas is passed through water containing finely-divided chalk in suspension, whilst the hydrochloric acid formed by the action of the chlorine upon the water is neutralized by the chalk, the **hypochlorous acid** produced at the same time remains uncombined:

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + 2HOCl + CO_2.$$

* To the view that the weakness of, e.g., HOCl may be attributed to the fact of its being a derivative of water it might be objected that potassium and sodium hydroxides, being likewise derivatives of water, are strong bases. The cases, however, are not parallel, since the halogen has to cause the separation of H ions and the alkali metal of OH ions. No single element, indeed, in combination with hydroxyl alone is known to form a powerful oxyacid. The presence of adjacent negative atoms or groups combined with an element is necessary before any considerable separation of hydrogen ions occurs.

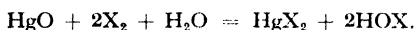
If sodium sulphate is substituted for calcium carbonate the reaction may be represented as follows:

$$Na_2SO_4 + Cl_2 + H_2O = NaHSO_4 + NaCl + HOCl;$$

the fixation of the hydrochloric acid by reaction with Na_2SO_4 allowing of the formation of HOCl in quantity. Hypochlorous acid may be conveniently prepared in solution by distilling a hypochlorite with dilute nitric acid; or by saturating bleaching-powder solution with chlorine, and distilling after displacing excess of chlorine by air:

$$Ca(OCl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4HOCl.$$

A general method for the preparation of acids of the type HOX consists in digesting the halogen and water with precipitated mercuric oxide, the following reaction taking place:

$$HgO + 2X_2 + H_2O = HgX_2 + 2HOX.$$

If excess of mercuric oxide is employed, an insoluble basic halide is formed, and a pure solution of the acid obtained by filtration, thus:

$$2HgO + 2X_2 + H_2O = HgO \cdot HgX_2 + 2HOX.$$

The oxide of mercury serves the purpose of removing the HX acid from the system, the HOX acids not being sufficiently strong to form salts with this oxide.

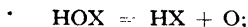
Owing to their instability none of these acids has been obtained pure; but solid **calcium hypochlorite** results when chlorine is passed into milk of lime, and the resulting solution is evaporated under reduced pressure. The dried salt is more efficient than bleaching-powder.

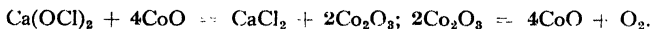
Sodium hypochlorite * has been obtained by passing chlorine into concentrated sodium hydroxide solution, cooled in ice water. After separation of sodium chloride, hair-like crystals of the hydrated salt are formed at $-10°$. These are probably NaOCl, $7H_2O$, but the pentahydrate NaOCl, $5H_2O$

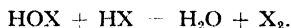
* Applebey, *Chem. Soc. Trans.* (1919), **115**, 1106.

is obtained when these crystals are melted at 18–19°, and the solution is then cooled to 10°.

The stability of acids of the type HOX diminishes from chlorine to iodine, just as the stability of the hydracids themselves diminishes. Hypoiodous acid is, however, much less stable than the other two, and cannot be distilled. The instability of these acids depends first of all upon a tendency to split off oxygen thus

$$HOX = HX + O;$$

the preparation of this gas from bleaching-powder by the catalytic action of cobaltous oxide depends on this reaction:

$$Ca(OCl)_2 + 4CoO = CaCl_2 + 2Co_2O_3;\ 2Co_2O_3 = 4CoO + O_2.$$

Hydracid also separates halogen in the following way:

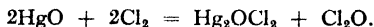
$$HOX + HX = H_2O + X_2.$$

The acids themselves, therefore, may yield halogen as well as oxygen by spontaneous decomposition, but when liberated from their salts by excess of halogen acid, halogen only will be evolved. Instead, however, of being evolved in the gaseous state, the oxygen liberated in the decomposition of HOX acid may oxidize the acid itself, producing a higher oxyacid of the type $HOXO_2$. Salts of these acids especially are produced when alkali hypochlorites are decomposed by heat, there being no free hydracid to cause evolution of halogen; thus:

$$3NaOX = NaOXO_2 + 2NaX.$$

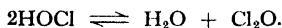
This tendency towards the formation of salts of the type $MOXO_2$ is increased by excess of halogen, and diminished by excess of alkali. The formation of chlorate by the action of excess of chlorine accounts for the occasional spoiling of bleaching-powder in the process of manufacture.

The tendency of hypoiodite to pass into iodide and iodate is much greater than in the case of the corresponding chlorine and bromine compounds, as will be seen later.

Anhydrides of the type X_2O.—The **monoxides,** Cl_2O, and Br_2O, are the only compounds of this type which exist; and just as hypochlorous acid is prepared by the action of chlorine on mercuric oxide and water, so its anhydride is formed when chlorine reacts with dry mercuric oxide, thus:

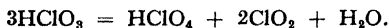
$$2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O.$$

Bromine monoxide is prepared similarly.

Chlorine monoxide is an unstable gas which yields hypochlorous acid with water. Distinct though small quantities of Cl_2O are present in aqueous solution, so that there exists the equilibrium:

$$2HOCl \rightleftharpoons H_2O + Cl_2O.$$

Fluorine monoxide does not behave as an anhydride.

The non-formation of iodine monoxide may be connected with the less stability of hypo-iodous acid, as compared with hypochlorous acid; in this case the anhydrides are less stable than the corresponding acids, though this is by no means generally the case. Sulphur dioxide, for instance, is more stable than sulphur trioxide, though sulphuric is much more stable than sulphurous acid. Carbonic and chromic anhydrides are likewise much more stable than the corresponding acids. There appears, therefore, to be no simple connection between the stabilities of an acid and its anhydride.

Dioxides XO_2.—All, except fluorine, form dioxides. **Chlorine dioxide** or **peroxide** is a heavy, dark-yellow explosive gas, which results from the self-oxidation and reduction of chloric acid, liberated from a chlorate by strong sulphuric acid:

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

A safer method for preparing the gas is to substitute oxalic for sulphuric acid. The solution of this gas in water is yellow and unstable, and contains the hydrate ClO_2, $8H_2O$. When dissolved in alkali, ClO_2 forms chlorite and chlorate thus:

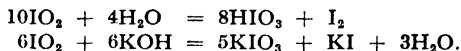
$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O.$$

On account of this reaction, ClO_2 has some claim to be considered the mixed anhydride of chlorous and chloric acids.

Iodine dioxide * is formed by heating iodic acid with concentrated sulphuric acid until evolution of iodine begins to accompany that of oxygen:

$$4HIO_3 = 2H_2O + 4IO_2 + O_2.$$

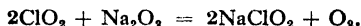
The pure compound is a lemon-yellow solid, decomposing into iodine pentoxide and iodine at 130°. Its reactions with hot water and aqueous alkali are as follows:

$$10IO_2 + 4H_2O = 8HIO_3 + I_2$$
$$6IO_2 + 6KOH = 5KIO_3 + KI + 3H_2O.$$

Thus IO_2 does not appear to resemble ClO_2 in anhydride character, probably because it is really a basic salt of tervalent iodine $OI(IO_3)$.

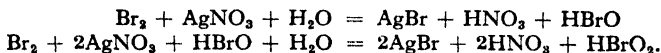
Acids of the Type HOXO

Chlorous acid, $HClO_2$, is itself unknown, but some of its salts can be prepared.

Besides being produced in the reaction between chlorine dioxide and sodium hydroxide, sodium chlorite is formed when an aqueous solution of the former is added to sodium peroxide, mutual reduction with evolution of oxygen resulting in the formation in solution of chlorite only:

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2.$$

Several solid chlorites are known, but they are very unstable.

Bromous acid, $HBrO_2$, is said to be formed † when bromine is added to saturated silver nitrate solution, thus:

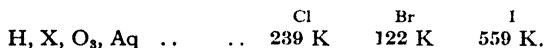
$$Br_2 + AgNO_3 + H_2O = AgBr + HNO_3 + HBrO$$
$$Br_2 + 2AgNO_3 + HBrO + H_2O = 2AgBr + 2HNO_3 + HBrO_2.$$

Acids of the type $HOXO_2$ (Chloric, Bromic, and Iodic Acids) and their Salts.—It has already been shown that

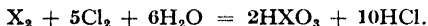
* Muir, *Chem. Soc. Trans.* (1909), **95**, 656.
† Richards, *J. Soc. Chem. Ind.* (1906), **25**, 4.

alkali salts of the type MOX readily pass into the more stable [$MOXO_2 + 2MX$] by self-oxidation and reduction thus:

$$3MOX = MOXO_2 + 2MX.$$

There does not appear to be much distinction between chlorine and bromine in respect to the above reaction, but in the case of iodine this reaction is much more rapid, taking place even in cold, dilute solution; for not only are the hypoiodites much less stable than the corresponding chlorine and bromine compounds, but the iodates are much more stable than the chlorates or bromates, as the following heats of formation show:

	Cl	Br	I
H, X, O_3, Aq	239 K	122 K	559 K.

Chlorine has no action on bromic or iodic acid, and these can be obtained by passing chlorine into bromine water, or into iodine suspended in water, the following reaction taking place:

$$X_2 + 5Cl_2 + 6H_2O = 2HXO_3 + 10HCl.$$

Chloride of bromine or iodine is probably first formed; this then yields hypobromous or hypoiodous and hydrochloric acids by the action of water, the chloranhydrides being thus hydrolyzed; the former then give bromic or iodic acid by spontaneous change.

Potassium bromate is also formed when chlorine is passed into a warm solution of potassium bromide and hydroxide, thus:

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O.$$

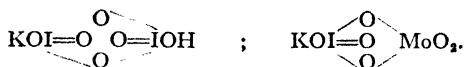
Chlorine, therefore, has no power to decompose potassium bromate.

The superior stability of iodic acid is shown by the fact that iodine displaces chlorine and bromine from chloric and bromic acids respectively, forming iodic acid. Potassium iodate may be obtained by heating iodine with potassium chlorate.

The reaction, however, which affords most striking evidence of the difference between iodic acid and the corresponding acids of chlorine and bromine is the direct oxidation of iodine

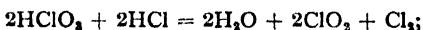
by nitric acid, with production of iodic acid in solution. This acid may be crystallized from its aqueous solution, whilst chloric and bromic acids are known only in such solution; and when heated to 170° it loses water and leaves **iodic anhydride**, I_2O_5, as a white, crystalline powder, which is decomposed into its elements at 300°.

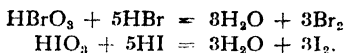
Iodic acid is further distinguished from chloric and bromic acids by the nature of some of its salts; for although the neutral alkali iodates are derivatives of a monobasic meta-acid, HIO_3, analogous to chloric and bromic acids, acid salts, such as KHI_2O_6 or KIO_3, HIO_3, and $KH_2I_3O_9$ or KIO_3, $2HIO_3$ are known. Moreover, molecular weight determinations show that in concentrated solution the free acid is $H_2I_2O_6$, and in dilute solution HIO_3. $H_2I_2O_6$ is dibasic, and comparable in strength with H_2SeO_4; but when it is neutralized by potash it produces not $K_2I_2O_6$ but $2KIO_3$. This acid forms a complex monobasic acid with molybdic anhydride, the analogy of whose potassium salt to potassium di-iodate is shown by the following formulæ:

$$KOI{=}O\overset{O}{\underset{O}{\quad}}O{=}IOH \quad ; \quad KOI{=}O\overset{O}{\underset{O}{\quad}}MoO_2.$$

When potassium di-iodate is neutralized in solution by one equivalent of potash, it breaks up into two molecules of KIO_3. Iodates show a marked contrast with chlorates in their solubility in water; for, whilst all chlorates are freely soluble, the iodates, with the exception of those of the alkalis, are sparingly soluble or insoluble.

Action of HXO_3 on HX Acids.—In general this action will involve an oxidation of the hydracid at the expense of the oxygen of the oxyacid. The nature of the reduction product will depend on the existence and stability of the lower oxides or oxyacids of the particular halogen considered.

In the case of chloric acid chlorine dioxide is the reduction product, and the reaction is as follows:

$$2HClO_3 + 2HCl = 2H_2O + 2ClO_2 + Cl_2;$$

but with bromic and iodic acids the element itself is liberated in each case, thus:

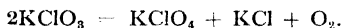
$$HBrO_3 + 5HBr = 3H_2O + 3Br_2$$
$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

It is necessary for the free acids to be present, the corresponding alkali salts having no action on one another.

Acids of the type $HOXO_3$.—The highest type of halogen oxyacid, $HOXO_3$, in which the halogen is septivalent, is represented by perchloric and periodic acids and their salts.

Perchloric acid is obtained, together with chlorine and oxygen, when attempts are made to concentrate an aqueous solution of chloric acid; and also when a strong solution of the latter acid is exposed to sunlight. Likewise, when potassium chlorate is carefully heated it may be transformed into perchlorate according to the reaction

$$4KClO_3 = 3KClO_4 + KCl,$$

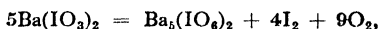
although there is generally loss of oxygen according to the reaction

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Further, when sulphuric acid acts upon an alkali chlorate perchloric acid results, together with chlorine dioxide; but when potassium perchlorate is heated with sulphuric acid, perchloric acid distils. These facts illustrate the superior stability of perchloric acid and the perchlorates, and thus a progressive rise of stability can be traced in the chlorine oxyacids from hypochlorous to perchloric acid. Aqueous solutions of perchloric acid and its salts are so stable as to resist reduction by hydrochloric and sulphurous acids; the anhydrous acid is, however, unstable, and explodes with violence on contact with oxidizable bodies. It is therefore perchlorate ions which manifest this stability, and not the free acid. Perchloric acid forms several hydrates, of which the monohydrate $HClO_4$, H_2O, is crystalline at atmospheric temperature. The **anhydride** of this acid, Cl_2O_7, has been

obtained by leaving the anhydrous acid in contact with phosphoric oxide kept below $-10°$. It is a colourless oil, boiling at 82°, which explodes on percussion.

Perbromic acid and its anhydride have not been obtained. When attempts are made to prepare the acid or its salts, by methods analogous to those which yield perchlorates, a bromide or oxide results, with evolution of oxygen, or bromine and oxygen.

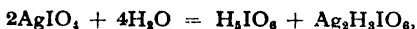
Periodic acid is formed by the action of iodine on an aqueous solution of perchloric acid, and by the electrolytic oxidation of iodic acid. It crystallizes with two molecules of water, $HIO_4, 2H_2O$. Crystallized perchloric acid contains one molecule of water, but this important difference exists between these two hydrates: that whereas only salts of meta-perchloric acid exist, so that the molecule of water in the crystalline acid must be regarded simply as water of crystallization, in the case of periodic acid salts of a pentabasic acid are well known, and therefore the formula must be written H_5IO_6. The barium salt of this acid is obtained by the ignition of barium iodate:

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2,$$

whence the free acid may be obtained in solution by precipitating the barium with the requisite amount of sulphuric acid.

The nature of periodic acid is further shown by the following reactions. When sodium iodate is oxidized by cold dilute nitric acid, silver nitrate precipitates from the solution the salt $Ag_2H_3IO_6$, and when this salt is dissolved in hot dilute nitric acid, and the solution evaporated on the water bath, crystals of the salt $AgIO_4$ separate, the removal of Ag_2O by the nitric acid causing the silver salt of the meta-acid to be formed thus:

$$2Ag_2H_3IO_6 + 2HNO_3 = 2AgIO_4 + 2AgNO_3 + 4H_2O.$$

This metasalt is acted on by water, however, in this way:

$$2AgIO_4 + 4H_2O = H_5IO_6 + Ag_2H_3IO_6,$$

a reaction which is in accord with the fact that when periodic acid crystallizes freely from water it is the form H_5IO_6 and not HIO_4 which separates.

It is possible, however, to dehydrate H_5IO_6 by heat so as to produce HIO_4. This cannot be done under ordinary pressure, for the acid begins to decompose at 110° into iodic acid, oxygen, and water vapour; * but under a pressure of 12 mm. H_5IO_6 is gradually transformed into HIO_4; the anhydride I_2O_7 has not, however, been obtained.

The following silver periodates can be precipitated from a periodate solution in presence of nitric acid of different concentrations: † $Ag_2H_3IO_6$; Ag_2HIO_5; $AgIO_4, H_2O$, which can be dehydrated at 130°; and the diperiodates $Ag_4I_2O_9, 3H_2O$, $Ag_4I_2O_9, H_2O$, and $Ag_4I_2O_9$. The even more complex salts $M^{\cdot}_8I_2O_{11}$, and $M^{\cdot}_{12}I_2O_{13}$ are known.

The derivation of the various periodic acids is shown in the following scheme. The nomenclature is that of Kimmins.‡

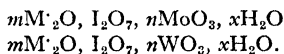
I_2O_7		unknown anhydride
$I_2O_6(OH)_2$	$= 2IO_3OH$ or HIO_4	metaperiodic acid
$I_2O_5(OH)_4$	or $H_4I_2O_9$	dimesoperiodic acid
$I_2O_4(OH)_6$	$= 2IO_2(OH)_3$ or H_3IO_5	mesoperiodic acid
$I_2O_3(OH)_8$	or $H_8I_2O_{11}$	diparaperiodic acid
$I_2O_2(OH)_{10}$	$= 2IO(OH)_5$ or H_5IO_6	paraperiodic acid
$I_2O(OH)_{12}$	or $H_{12}I_2O_{13}$	——
$I_2(OH)_{14}$	$= 2I(OH)_7$	unknown orthoacid.

The soluble salts of the polybasic periodic acids suffer hydrolysis in water, and give an alkaline reaction with litmus. They share this property with other polybasic acids such as phosphoric acid. They may also be considered as basic salts; for instance, Na_5IO_6 may be written $NaIO_4, 2Na_2O$.

Periodic acid and its salts are more stable than their chlorine analogues. The hydroxylation of the anhydride beyond the meta- stage, in the oxyacids of this group, occurs only with

* Lamb, *Amer. Chem. J.* (1902), **27**, 134.
† Kimmins, *Chem. Soc. Trans.* (1887), **51** 367,
‡ *Chem. Soc. Trans.* (1889), **55**, 148.

periodic acid, though the existence of $H_2I_2O_8$ shows a doubling of the molecule. Periodic resembles iodic acid in forming complex acids and salts with molybdic and tungstic anhydrides of the general types

$$mM'_2O, I_2O_7, nMoO_3, xH_2O$$
$$mM'_2O, I_2O_7, nWO_3, xH_2O.$$

Relative strengths of the halogen oxyacids.—Little can be said on this subject beyond the statement that acids of the type HOX are exceedingly weak, as indeed appears above, and that the strength of the acids increases with the addition of oxygen. Chloric acid, for instance, is known to be nearly as strong an acid as hydrochloric, and the same relationship is probably true in the case of the oxyacids of bromine and iodine.

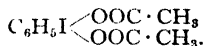
Certain Other Iodine Derivatives

Iodine, in distinction from the other halogens, forms several types of organic derivatives in which the element is polyvalent; and these compounds, by virtue of their properties and constitution, suggest analogies between iodine and nitrogen as well as some other elements in the fifth and sixth groups of the periodic system.

Iodine trichloride, ICl_3, a yellow crystalline substance, formed by the action of chlorine on the red monochloride, or of liquid chlorine on iodine, is very unstable, easily decomposing again into ICl and Cl_2. It is slowly decomposed by water and alkalis into hydriodic, iodic, hydrochloric, and chloric acids or their salts, so that iodous acid, of which iodine trichloride is the chloranhydride, and the alkali iodites are unknown.

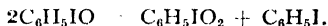
If an atom of iodine is associated with the phenyl radicle C_6H_5, the iodobenzene thus resulting, like iodine monochloride, is capable of combining with two atoms of chlorine, forming phenyl iodosochloride, $C_6H_5ICl_2$, in which the iodine atom is trivalent; this body is decomposed by dilute aqueous alkali,

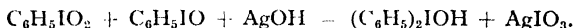
with the separation of the oxide **iodosobenzene**, $C_6H_5I=O$, whose basic properties are shown by its combination with glacial acetic acid, forming the acetate,

$$C_6H_5I\left\langle\begin{matrix}OOC\cdot CH_3\\OOC\cdot CH_3.\end{matrix}\right.$$

This compound also possesses oxidizing properties, owing to the ease with which its oxygen atom is split off. Iodine, for instance, is liberated by iodosobenzene from hydriodic acid,

$$C_6H_5IO + 2HI = C_6H_5I + H_2O + I_2;$$

and this compound undergoes self-oxidation and reduction when treated with steam, thus:

$$2C_6H_5IO = C_6H_5IO_2 + C_6H_5I.$$

The oxidation product is **iodobenzene**, or **iodoxybenzene**, which yields up all its oxygen in reaction with hydriodic acid, and also reacts with iodosobenzene and silver oxide in the following manner:

$$C_6H_5IO_2 + C_6H_5IO + AgOH = (C_6H_5)_2IOH + AgIO_3.$$

The product is **diphenyliodonium hydroxide**, a base which is soluble in water, showing a strongly alkaline reaction, and is thus a derivative of hypothetical iodonium hydroxide, IH_2OH, which is comparable in type with hydroxylamine, NH_2OH. The salts of substituted **iodonium bases** are more nearly related in properties, however, to ammonium compounds.

Theoretical considerations.—It will be of interest to inquire how far the existence of these iodonium compounds, which were discovered by Victor Meyer, might be suggested by analogies furnished by the periodic law. It has been shown previously that the analogues of ammonium in the fifth group are phosphonium, arsonium, and stibonium respectively, only the alkyl derivatives of the two latter basic radicles being known; and that bismuth alkyls, although known, are devoid of basic properties.

Analogues of these compounds exist in the sixth group in

the sulphonium derivatives, which are related to hydrogen sulphide as ammonium derivatives are related to ammonia. Since, however, hydrogen sulphide possesses slightly acidic properties, it is only when the hydrogen is replaced by alkyl groups that bases can be formed. Triethylsulphonium hydroxide, $(C_2H_5)_3SOH$, is a powerful base which displaces ammonia from its salts. Analogous selenium and tellurium bases and their salts exist; suitable salts of all three display optical activity.

In the seventh group the two conditions, of comparative electro-positiveness of element and sufficient stability of hydride and its derivatives, are realized only in the case of iodine. Of course hydrogen iodide is no more able to combine with acids to form iodonium salts than hydrogen sulphide to form sulphonium compounds, and, as in the case of arsonium, stibonium, and sulphonium, as well as oxonium derivatives, it is only those in which the hydrogen atoms are replaced by hydrocarbon radicles which exist. The following diagram sets forth these considerations, power to form basic radicles being limited as indicated by the dotted lines *ab* and *bd*:

Gp. V B	Gp. VI B	Gp. VII B
XR_4OH	XR_3OH	XR_2OH
a N	O	F
P	S	Cl
As	Se	Br
Sb d	Te	b I
Bi	—	—

Nitrogen, sulphur, and iodine, together with phosphorus, arsenic, and antimony, and to a less extent oxygen as well as selenium and tellurium, form the basic radicles under discussion. Fluorine, chlorine, and bromine are too electro-negative to do so; bismuth too electro-positive.

Now although bismuth forms no derivatives of the type BiR_4OH, since its affinity for oxygen increases as that for hydrogen diminishes, it may be expected to form bases in which some of the hydrogen or hydrocarbon residues are replaced by oxygen; and $Bi(C_2H_5)O$ is a base which forms a nitrate, $BiC_2H_5(NO_3)_2$.

Similar compounds of sulphur, selenium, and tellurium exist, and increase in basic properties from sulphur to tellurium. The three following compounds illustrate this principle:

Diethylsulphoxide $(C_2H_5)_2SO$, feebly basic, liberated from its salts by $BaCO_3$.

Diethylselenoxide $(C_2H_5)_2SeO$, a stronger base than the foregoing.

Diethyltelluroxide $(C_2H_5)_2TeO$, a strong base, possessing an alkaline reaction, and displacing ammonia from its salts.

Combination with an additional oxygen atom is exemplified in the sixth group by the sulphones, e.g. diethylsulphone, $(C_2H_5)_2SO_2$. *A priori*, these bodies might be expected either to be basic peroxides, if the second oxygen is feebly attached, or neutral bodies if stable. The sulphones are, in fact, neutral substances which are very stable.

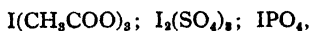
The properties of iodoso- and iodobenzene will now be understood in the light of the above remarks.

Iodosobenzene, C_6H_5IO, is feebly basic, like diethylsulphoxide; and iodobenzene, $C_6H_5IO_2$, behaves as a basic peroxide.

The presence of the phenyl rather than the ethyl group in these basic compounds is, however, remarkable, since this radicle generally confers acidic properties, as is shown in the comparison of phenol, C_6H_5OH, with ethyl alcohol, C_2H_5OH.

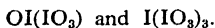
These considerations show, nevertheless, that in the formation of iodonium and allied compounds iodine manifests properties which might be expected from the position which it occupies in the periodic system.

That iodine may exhibit basic character has already been noted in the polyhalides of Group I A elements: basic tervalent iodine occurs in ICl_3 and in the salts:

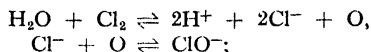
$$I(CH_3COO)_3;\ I_2(SO_4)_3;\ IPO_4,$$

and univalent iodine forms

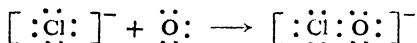
$$[C_5H_5N \rightarrow I \leftarrow NH_5C_5]NO_3.$$

The dioxide, IO_2 or I_2O_4, is regarded as a basic iodate, and the oxide I_4O_9 as a normal iodate of tervalent iodine, thus:

$$OI(IO_3) \text{ and } I(IO_3)_3.$$

The other halogens do not give such compounds, but there is evidence that they may evince basic character in their reactions.

The reaction between chlorine and water may be due to the formation and oxidation of chloride ions, thus:

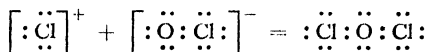
$$H_2O + Cl_2 \rightleftharpoons 2H^+ + 2Cl^- + O,$$
$$Cl^- + O \rightleftharpoons ClO^-;$$

for whilst a chlorine atom cannot combine with an oxygen atom, it may be supposed that a chloride ion can:

$$[:\ddot{\underset{..}{Cl}}:]^- + \ddot{\underset{..}{O}}: \longrightarrow [:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}:]^-$$

There is, however, no experimental evidence for this. A modern way of regarding this reaction is to suppose that the Cl_2 molecule is polar, or at least can divide unsymmetrically, and so react with water thus: $\overset{+}{Cl}Cl+\overset{+}{H}\overset{-}{OH}=\overset{+}{H}\overset{-}{Cl}+\overset{-}{HO}\overset{+}{Cl}$.

From the fact that Cl_2O exists in aqueous hypochlorous acid, it has been inferred that the acid dissociates in two ways, thus:

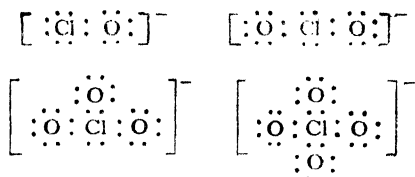
$$Cl^+ + OH^- \rightleftharpoons HOCl \rightleftharpoons H^+ + OCl^-.$$

Chlorine monoxide would then result:

$$[:\ddot{\underset{..}{Cl}}]^+ + [:\ddot{\underset{..}{O}}:\ddot{\underset{..}{Cl}}:]^- = :\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}:\ddot{\underset{..}{Cl}}:$$

Nevertheless HOCl mainly ionizes as an acid and not as a base as these considerations would suggest.

The electronic formulæ for the ions of the chlorine oxy acids are as follows:

$$\left[:\ddot{\text{Cl}}:\ddot{\text{O}}:\right]^- \qquad \left[:\ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}:\right]^-$$

$$\left[\begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}: \end{array}\right]^- \qquad \left[\begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}: \\ :\ddot{\text{O}}: \end{array}\right]^-$$

Hydrated perchloric acid $HClO_4, H_2O$ is probably hydroxonium perchlorate, $[OH_3]^+ClO_4$. From concentrated nitric acid Hantzsch (1925) has obtained similar perchlorates, e.g. $[(HO)_2NO]ClO_4$. Pentabasic periodic acid, $HIO_4, 2H_2O$, is, however, $(HO)_5I{\rightarrow}O$, the oxygen atoms being attached directly to iodine, which thus has a valency shell of twelve electrons, i.e. seven of its own, and five from the ionizable hydrogen atoms. (Cf. $Te(OH)_6$).

Other Halogen Oxides.—The oxide F_2O (*vide* p. 424) can be prepared by passing fluorine through dilute KOH solution.

Fluorine and oxygen unite directly at low pressure and temperature under an electric discharge to give F_2O_2, a brown gas which forms a yellow solid below $-160°$ C. It decomposes irreversibly above $-100°$ C. to give colourless FO, a gas which oxidizes potassium iodide to iodine.

Chlorine hexoxide, Cl_2O_6, forms a red oil (M.P $-1°$ C.) when light acts on ClO_2, or on a mixture of chlorine and ozone. It exists in equilibrium, thus: $Cl_2O_6 \rightleftharpoons 2ClO_3$, and behaves as a mixed anhydride forming $HClO_3$ and $HClO_4$ with water.

Chlorine tetroxide, $(ClO_4)_2$, forms in ether solution thus:

$$2AgClO_4 + I_2 = 2AgI + (ClO_4)_2.$$

It unites directly with metals forming salts, e.g. $CuClO_4$.

The less stable **iodine tetroxide** is formed similarly.

The **oxide** $\mathbf{(Br_3O_8)_n}$ is a white crystalline solid formed by a low-pressure mixture of pure ozone and bromine vapour at 0° C. It is dimorphous and unstable, and with water yields an oxidizing solution (Schumacher, 1929).

MANGANESE

For a long time manganese was the only representative of sub-group VII A of the periodic classification. Two higher analogues of this element, however, exist, masurium (Ma) and rhenium (Re), discovered in 1925. The similarity between manganese and the halogens is very slight, as might be expected from the fact that these elements are members of an extreme group. The resemblance is confined, indeed, to the highest oxide, Mn_2O_7, and its derivatives; for only when thus combined with the maximum proportion of oxygen does manganese exhibit acidigenic properties at all comparable with those possessed by the halogens. Permanganic acid, $HMnO_4$, is thus analogous to perchloric acid, $HClO_4$, and potassium permanganate is isomorphous with potassium perchlorate. When, however, these compounds are reduced, so that the type, R_2O_7, from which they are derived, is departed from, the similarity at once ends; for whilst chlorine maintains its electro-negative character in compounds containing no oxygen, manganese exhibits relationship with its neighbours in the periodic table, chromium and iron, and in its lowest oxidized state yields compounds in which the element is entirely basigenic.

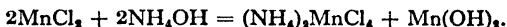
Thus manganates, $M^{\cdot}_2MnO_4$, are isomorphous with chromates, $M^{\cdot}_2CrO_4$, so that MnO_3 is analogous to CrO_3; manganic alum, $(NH_4)_2SO_4$, $Mn_2(SO_4)_3$, $24H_2O$, is isomorphous with $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$, thus showing an analogy between Mn_2O_3 and Fe_2O_3; and, further, certain manganous and ferrous salts form isomorphous double salts with alkali metals, so that MnO and FeO are analogous oxides.

With regard to the elements themselves, the contrast between manganese, a hard brilliant metal with a high melting-point, and chlorine, a typical halogen, is very great; whilst the relationship between metallic manganese and chromium and iron is very close.

SUMMARY OF THE OXIDES OF MANGANESE

MnO, a basic oxide yielding manganous salts.
Mn_3O_4, a very stable neutral oxide; probably a salt.
Mn_2O_3, a feebly basic oxide giving rise to manganic salts.
MnO_2, possesses feebly acidic properties; a basic peroxide.
MnO_3, an acidic oxide—manganic anhydride.
Mn_2O_7, an acidic oxide—permanganic anhydride.

Manganous oxide, MnO, and its salts.—MnO is a greyish-green powder which readily oxidizes in air to Mn_3O_4; $Mn(OH)_2$, a reddish-white precipitate quickly oxidizing to hydrated Mn_2O_3. Manganous hydroxide is not quite insoluble in water, and it is only partially precipitated by ammonia on account of the formation of an ammonium double salt which removes manganous ions from the solution:

$$2MnCl_2 + 2NH_4OH = (NH_4)_2MnCl_4 + Mn(OH)_2.$$

For the same reason the precipitation of manganous hydroxide by ammonia is completely prevented by the presence of ammonium salts. From such an alkaline solution, however, manganic hydroxide is slowly separated by atmospheric oxidation.

The **manganous salts** are pale pink, their solutions being almost colourless. They are stable in the solid state and in neutral or acid solution, differing in this respect from ferrous salts. The **chloride** crystallizes with 2, 4, and 6 H_2O, that with $4H_2O$ being in two modifications, one of which is isomorphous with $FeCl_2$, $4H_2O$; it forms numerous double salts. The **sulphate** crystallizes with 1, 4, 5, or 7 H_2O, according to temperature. $MnSO_4$, $5H_2O$ is isomorphous with $CuSO_4$, $5H_2O$; $MnSO_4$, $4H_2O$, and $MnSO_4$, $7H_2O$ with the corresponding hydrates of $FeSO_4$; $MnSO_4$, H_2O is produced by exposure of the other hydrates to dry air. Manganese sulphate also forms double salts with the sulphates of the alkali metals and ammonium, containing 2, 4, or 6 H_2O; e.g. $MnSO_4$, Na_2SO_4, $2H_2O$; $MnSO_4$, K_2SO_4, $4H_2O$; $MnSO_4$, $(NH_4)_2SO_4$, $6H_2O$.

Manganous sulphide, MnS, obtained mixed with sulphur

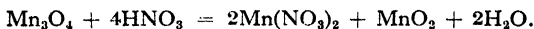
by precipitating a manganous salt with ammonium sulphide, is a flesh-coloured precipitate soluble in even acetic acid. In contact with excess of precipitant it passes into a green crystalline form, which can also be produced in the dry way. Besides this green form there appear to be red and grey modifications, and the flesh-coloured precipitate may be a mixture of these.

Mangano-manganic oxide, Mn_3O_4, occurs as a dark-red powder, which is very stable at high temperatures, and is formed when any of the other oxides is ignited in the air.

Mn_3O_4 is not a simple basic oxide giving rise to a series of salts; its behaviour towards acids shows it to be a compound oxide, whose composition may be either MnO, Mn_2O_3 or $2MnO, MnO_2$. It will be useful to compare this oxide with the apparently analogous oxides Pb_3O_4 and Fe_3O_4.

There is little doubt that the oxide Pb_3O_4 may be considered as $2PbO, PbO_2$. Fe_3O_4, however, must be considered to be FeO, Fe_2O_3, since no dioxide in which iron is quadrivalent is known to exist. Moreover, a hydrated artificial form of this oxide may be prepared by precipitating a mixture of ferrous and ferric salts with caustic alkali.

In the case of Mn_3O_4, therefore, a correct view of its constitution depends upon the nature of the oxide Mn_2O_3. This will be discussed below; meanwhile the following reactions of Mn_3O_4 may be stated. This oxide dissolves slowly in cold concentrated sulphuric acid, forming a red solution which contains both manganous and manganic sulphates. Acetic acid and boiling ammonium-chloride solution remove MnO, leaving Mn_2O_3. So far the constitution, MnO, Mn_2O_3, is upheld. On heating, however, with dilute sulphuric acid or with nitric acid, manganous salt and MnO_2 are formed:

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

This reaction supports the constitution, $2MnO, MnO_2$.

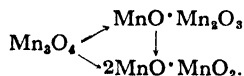
Manganic oxide, Mn_2O_3, may be obtained as a black powder by heating the other oxides in a current of oxygen. The corresponding hydroxide, $MnO{\cdot}OH$, is formed when

manganous hydroxide oxidizes in the air, and also when manganic sulphate is decomposed by water. The behaviour of this oxide or hydroxide towards acids is significant. The hydroxide dissolves in cold hydrochloric acid, forming a dark-brown solution, which evolves chlorine when heated. In all probability this solution contains $MnCl_3$. Neither the oxide nor hydroxide dissolves to any extent in cold sulphuric acid. Hot strong nitric acid, however, dissolves the hydroxide, forming manganous nitrate and precipitating the dioxide:

$$2MnO \cdot OH + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

Manganic salts are very unstable, and are decomposed by water. **Manganic alums** crystallize at low temperatures from mixed solutions of manganic acetate and alkali sulphates in sulphuric acid, and are also obtained by anodic oxidation of mixed solutions of manganous and alkali sulphates. Owing to its sparing solubility the cæsium alum is the easiest to prepare. Crystallized manganic alums are red, and their solutions in sulphuric acid are violet, but turn red on dilution, and then separate brown $Mn(OH)_3$.

These facts point to the conclusion that manganic oxide and hydroxide possess basic functions and a constitution corresponding thereto, but that on heating with acids a separation takes place into MnO, which dissolves, and MnO_2, which is precipitated. The constitution of Mn_3O_4 and the reactions involving the separation of MnO_2 may be represented in accordance with this view as follows:

$$Mn_3O_4 \begin{array}{l} \nearrow MnO \cdot Mn_2O_3 \\ \qquad\quad \downarrow \\ \searrow 2MnO \cdot MnO_2. \end{array}$$

The combination of Mn_2O_3 with MnO suggests the possession of feebly acidic properties by the former oxide. Similarly, manganic chloride, $MnCl_3$, should possess some of the properties of a chloranhydride. This is shown probably to be the case by the solubility of this compound in ether and absolute alcohol, and more particularly by its combination

with alkali chlorides (to form, e.g. K_2MnCl_5), and the hydrochlorides of certain organic bases to form compounds of the type $MnCl_3$, 2RHCl. The isomorphism of these with corresponding iron salts bears out the analogy between Mn and Fe; though ferric salts are much more stable than manganic salts.

Manganese dioxide or peroxide, MnO_2.—This oxide, well known on account of its use in the manufacture of chlorine, is of a dark brown or black colour.

Precipitated hydrated manganese dioxide, obtained by adding alkaline hypochlorite to the solution of a manganous salt, just as PbO_2 is obtained from a lead salt, easily passes into the colloidal state, producing a brown liquid, which is acid in reaction. Such a liquid appears to contain manganous acid, H_2MnO_3, or H_4MnO_4. A similar solution is produced transitorily in the titration of hot acidified oxalic-acid solution with permanganate, and is well seen when a drop of permanganate is added to warm oxalic-acid solution. Various compounds of MnO_2 with basic oxides are known. $K_2Mn_5O_{11}$ is a yellow powder, and $CaMn_5O_{11}$ is a dark-brown precipitate formed by pouring manganous nitrate solution into excess of bleaching-powder solution. The manganese mud formed by the oxidation of manganous hydroxide in the presence of lime in the Weldon recovery process contains a calcium manganite; and the hydrated Mn_2O_3, produced by atmospheric oxidation of $Mn(OH)_2$, may be regarded as manganous manganite:

$$\begin{matrix}HO\\HO\end{matrix}\!\!>Mn<\!\!\begin{matrix}O\\O\end{matrix}\!\!>Mn.$$

It will thus be concluded that manganese dioxide possesses the properties of a feebly acidic anhydride. It is probably not a basic oxide, since it forms no oxysalts, i.e. no quadrivalent manganese ion exists. **Manganese tetrachloride, $MnCl_4$,** has, however, been obtained by the action of dry hydrogen chloride on manganese dioxide suspended in carbon tetrachloride. It is unstable, but forms complex salts, such as K_2MnCl_6.

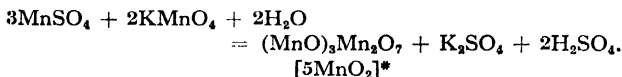
Manganese dioxide is not a superoxide in the sense of yielding hydrogen peroxide with acids, though it is said, when freshly precipitated, to dissolve in concentrated hydrogen peroxide solution at $-20°$, forming the manganous salt of hydrogen peroxide,

$$Mn\begin{smallmatrix}/O\\ |\\ \backslash O\end{smallmatrix};$$

and it is questionable whether this compound can be represented as a simple polyoxide having the constitution O=Mn=O. Reactions are known which appear to indicate the saline nature of this compound; for instance, the dioxide is precipitated, apparently as manganous manganate, when barium manganate and manganous sulphate interact:

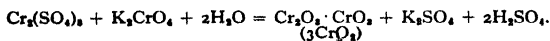
$$BaMnO_4 + MnSO_4 = MnMnO_4 + BaSO_4,$$

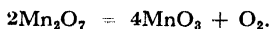
and is also formed by the action of potassium permanganate on manganous sulphate solution:

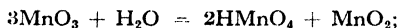
$$3MnSO_4 + 2KMnO_4 + 2H_2O = \underset{[5MnO_2]^*}{(MnO)_3Mn_2O_7} + K_2SO_4 + 2H_2SO_4.$$

The above reactions may, however, be regarded more simply as instances of oxidation of manganous salt with the corresponding reduction of manganate or permanganate to the dioxide stage. In any case the molecular constitution of manganese dioxide must remain undecided.

Manganese trioxide—Manganic anhydride, MnO_3.—This oxide, the anhydride of manganic acid, is unstable, and can only be obtained in small quantity. It is evolved as a pink fume, which may be condensed to a red, viscid mass, when a solution of potassium permanganate in concentrated sulphuric acid is dropped on to dry sodium carbonate.

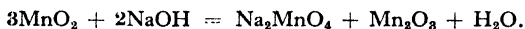
* This reaction occurs quantitatively only when a base, e.g. ZnO, is present to form manganite, and so cause all the manganese to assume the quadrivalent state. A seeming analogy to this reaction is furnished by the following:

$$Cr_2(SO_4)_3 + K_2CrO_4 + 2H_2O = \underset{(3CrO_2)}{Cr_2O_3 \cdot CrO_3} + K_2SO_4 + 2H_2SO_4.$$

The MnO_3 owes its existence to the spontaneous decomposition of permanganic anhydride, Mn_2O_7, as follows:

$$2Mn_2O_7 = 4MnO_3 + O_2.$$

Manganic anhydride is decomposed by water in the following manner:

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2;$$

from which it may be concluded that manganic acid is an unstable substance.

The Manganates.—Sodium manganate is formed by heating together manganese dioxide and caustic soda in air or with an oxidizing agent. In the absence of air the following reaction takes place:

$$3MnO_2 + 2NaOH = Na_2MnO_4 + Mn_2O_3 + H_2O.$$

The salt may be obtained in small crystals, having the composition $Na_2MnO_4, 10H_2O$, which are isomorphous with Glauber's salt. Manganates, derived from the acid H_2MnO_4, are known in the case of the metals Na, K, Rb, Co, Ag, Tl, Ca, Ba, Sr. They are bluish-green salts, and when soluble are isomorphous with sulphates, selenates, and chromates, so that an analogy between manganese and the members of the sixth group is established. The alkali manganates pass into permanganates by atmospheric oxidation thus:

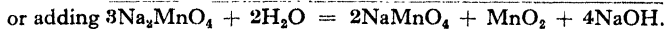
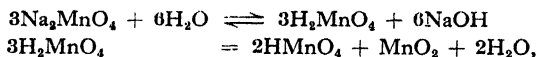
$$2Na_2MnO_4 + H_2O + O = 2NaMnO_4 + 2NaOH;$$

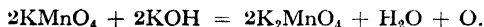
and since manganic acid itself, if formed, would decompose spontaneously into permanganic acid and manganese dioxide, as may be concluded from the action of water on its anhydride, any reaction which liberates this acid will cause such decomposition to take place.

Now when sodium manganate is dissolved in a little water a deep-green solution is obtained, which, on dilution with much water, or the addition of a little acid, turns pink, owing to the formation of permanganate. This is due to the fact that manganate is stable only in presence of excess of alkali, so

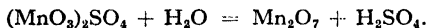
that when that excess is not present the salt is hydrolyzed and the resulting manganic acid undergoes self-oxidation and reduction thus:

$$3Na_2MnO_4 + 6H_2O \rightleftharpoons 3H_2MnO_4 + 6NaOH$$
$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O,$$

or adding $3Na_2MnO_4 + 2H_2O = 2NaMnO_4 + MnO_2 + 4NaOH.$

This reaction takes place in dilute solution even when a little alkali is present, but it is greatly promoted by the presence of acid, even of carbonic acid, which neutralizes the hydrolytic alkali. It is commonly observed that when a drop of permanganate solution is mixed with excess of alkali the colour passes from crimson through violet to green, permanganate being thus reduced to manganate. Such a reaction involves loss of oxygen thus:

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O.$$

This change is ordinarily due to the presence of oxidizable matter in the alkali; but when the reaction takes place in concentrated solution it is possible for oxygen gas to be expelled in the formation of the more stable manganate.

Manganese heptoxide — Permanganic anhydride, Mn_2O_7.—Potassium permanganate dissolves in concentrated sulphuric acid, forming an olive-green liquid. It is apparent from this change of colour that a chemical change has taken place, and it is believed that the solution contains the sulphate $(MnO_3)_2SO_4$. If a little water is added to this solution while it is kept cool, a dark reddish-brown liquid separates, which does not solidify at $-20°$. This is permanganic anhydride, formed by the decomposition of the sulphate in the following way:

$$(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4.$$

This compound is very unstable, easily decomposing into a lower oxide and oxygen, the evolved oxygen carrying with it violet fumes of the anhydride. It dissolves in water, forming a violet solution of permanganic acid, and in strong sulphuric

acid, with the regeneration of the above green sulphate. The existence of this sulphate recalls that of the uranyl salts, which are derived from uranic oxide, UO_3, by the replacement of one atom of oxygen by acidic radicles.

Permanganic acid, $HMnO_4$, and the **Permanganates.**— The solution obtained by decomposing barium permanganate with its equivalent of dilute sulphuric acid yields on slow evaporation violet-black crystals of permanganic acid, which are very unstable, easily decomposing into manganese dioxide, oxygen, and water.

Permanganic acid is formed in solution when a manganous salt in small quantity is oxidized by lead peroxide and nitric acid, bismuthic acid, or ammonium persulphate and acid in presence of silver nitrate as catalyst. These reactions are used for the detection or colorimetric estimation of small quantities of manganese.

Permanganic chloride, MnO_3Cl, is known; and, both as regards its manner of preparation, by the action of hydrogen chloride on **permanganic sulphate,** $(MnO_3)_2SO_4$, and its properties, including its reaction with water, it is shown to be a true acid chloride.

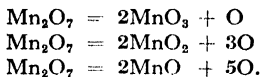
Potassium permanganate is the most important salt of permanganic acid. It is usually prepared by heating together caustic potash, potassium chlorate, and manganese dioxide, extracting with water, and passing CO_2 through the liquid to convert manganate into permanganate. The crystals of this salt consist of almost black rhombic prisms, with a green metallic lustre, which are isomorphous with potassium perchlorate. They yield a red powder, and dissolve in water, forming a deep-purple solution. This solution slowly decomposes in presence of traces of organic matter with separation of manganese dioxide. When solid $KMnO_4$ is heated to 240° it decomposes as follows:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

With concentrated sulphuric acid permanganic acid is first

separated, permanganic sulphate also being formed, and this breaks up on heating into manganese dioxide, oxygen, and water, manganous sulphate eventually resulting.

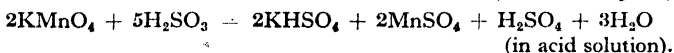
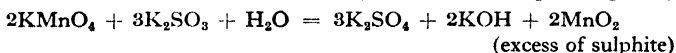
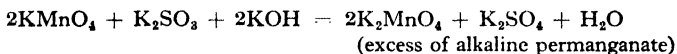
Potassium permanganate is a valuable oxidizing agent. Three stages in its reduction may be observed, the decomposition products being respectively potassium manganate, manganese dioxide, and a manganous salt. These changes may thus be represented in terms of oxides:

$$Mn_2O_7 = 2MnO_3 + O$$
$$Mn_2O_7 = 2MnO_2 + 3O$$
$$Mn_2O_7 = 2MnO + 5O.$$

The first reaction takes place in alkaline, the second in alkaline or neutral solution, the last generally in presence of free acid.

The following examples with sulphites are typical:

$$2KMnO_4 + K_2SO_3 + 2KOH = 2K_2MnO_4 + K_2SO_4 + H_2O$$
(excess of alkaline permanganate)

$$2KMnO_4 + 3K_2SO_3 + H_2O = 3K_2SO_4 + 2KOH + 2MnO_2$$
(excess of sulphite)

$$2KMnO_4 + 5H_2SO_3 = 2KHSO_4 + 2MnSO_4 + H_2SO_4 + 3H_2O$$
(in acid solution).

Although permanganate is easiest reduced to manganous salt in presence of acid which promotes the formation of such salt, it is possible to cause this reduction to take place in alkaline solution if a condition of stability of a manganous compound obtains. Thus if a drop of permanganate solution is added to excess of alkali sulphide the brown precipitate of hydrated manganese dioxide first formed soon passes into the paler and less soluble manganous sulphide; and if permanganate is similarly added to ammoniacal sulphite solution containing much ammonium chloride, the brown precipitate formed dissolves on boiling, with the production of a colourless solution containing manganous ammonium chloride.

The use of permanganate for titration of ferrous iron in presence of hydrochloric acid is avoided because the end-point is not sharp, and the results are likely to be high unless man-

ganese sulphate has been added. The explanation usually given of this irregularity is that the hydrochloric acid is oxidized by the permanganate; but Friend * has shown reason to believe that a higher chloride of manganese is formed and reacts with ferrous chloride until equilibrium is reached, according to the equation:

$$MnCl_{(2+x)} + xFeCl_2 \rightleftharpoons MnCl_2 + xFeCl_3.$$

Thus some manganese remains unreduced to manganous salt, and consequently too much permanganate is employed in the titration. That oxidation of hydrochloric acid is not the cause of the anomaly is shown by the fact that oxalic acid can be accurately titrated with permanganate in presence of sufficient hydrochloric acid, and that hydrofluoric acid has a disturbing effect in the iron titration somewhat similar to that of hydrochloric acid.

Permanganic acid is a strong acid, comparable with perchloric acid. Its salts are largely ionized in aqueous solution, and give an absorption spectrum characteristic of the permanganate ion.

Other permanganates are similar to the potassium salt, that of silver being the least soluble in water.

MASURIUM AND RHENIUM

The discovery of masurium (Ma) and rhenium (Re), the eka-manganese and dvi-manganese of Mendeléeff, is the result of Moseley's application of X-rays, firstly, as a method of fixing the position in the periodic classification of elements definitely missing, and secondly, as a ready means of identification. Guided by the periodic table, Noddack and his co-workers (1925) sought the missing group VII A elements of atomic numbers 43 and 75 in association with neighbouring transition elements, and by their X-ray spectra found them in platinum ores, in *tungstite*, WO_3, in *gadolinite*, $(FeBe)Y_2Si_2O_{10}$, and in the *columbites*, Fe(Mn) $[(Cb, Ta)O_3]_2$. *Molybdenum*

* *Chem. Soc. Trans.* (1909), 95, 1228.

glance, MoS_2, contains ReS_2. According to Loring and Druce (1925), rhenium may be obtained in small amount from crude manganese preparations. The elements are very rare; rhenium, the more abundant, being present up to one-millionth of the weight of ore.

Little is known of masurium, but rhenium is readily separated from the mineral residues by oxidation to per-rhenate and precipitation as the sparingly soluble salt, $KReO_4$. From molybdenum ores it may be separated as Re_2O_7, which is more volatile than MoO_3.

Rhenium undoubtedly finds its true position in series between tungsten and osmium, resembling the former in the formation of oxyhalides, while the reduction of its compounds to the free element, which is a catalyst, recalls the platinum metals rather than manganese. The salt, $K_4[Re_2OCl_{10}]$, forms mixed crystals with the corresponding ruthenium salt. The oxidation of the metal by nitric acid to per-rhenic acid resembles the formation of HIO_3 from iodine, and a further analogy to iodine is offered by the meso-perrhenates. It shows distinct relationship to manganese in the stable ReO_2, $2H_2O$ and the rhenites, comparable to MnO_2 and the manganites, but differs therefrom in the stability of the heptoxide, the formation of a heptasulphide, and the non-existence of ReO and stable bivalent salts.

Rhenium exhibits valencies of 3, 4, 5, 6 and 7; lower valencies probably exist but are unstable. The emergence of quinquivalency, unknown in manganese, is notable. In alkaline solution, compounds of intermediate valency tend to undergo oxidation and reduction, e.g.

$$3Re^{V} \rightleftharpoons 2Re^{IV} + Re^{VII}.$$

The metal is obtained as a grey powder resembling platinum by reducing per-rhenates, oxides, or sulphides, by hydrogen. Unlike manganese, it is stable in air. It is inert to HCl and HF, is slowly attacked by H_2SO_4, and with HNO_3 yields per-rhenic acid, $HReO_4$. It is stable to fused alkali in absence

of air; with air present it undergoes oxidation with intermediate colour changes to the white septivalent stage.

Tabulated below are some physical properties of rhenium and neighbouring elements.

	W	Re	Os	Mn
Dens.	18·72	21·9	22·48	7·85
At. vol.	9·8	8·8	8·5	7·4
M.P.	3260°	3160°	2500°	1260°

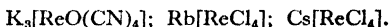
The following **oxides** are known:

Re_2O_3, xH_2O; feebly basic.
ReO_2; acidic giving rhenites.
ReO_3; acidic giving rhenates.
Re_2O_7; acidic giving per-rhenates.

Rhenium sesquioxide, Re_2O_3, is produced in hydrated form when $ReCl_3$ is hydrolyzed by alkali. It oxidizes readily.

The **trihalides,** $ReCl_3$ and $ReBr_3$ are known. Rhenium trichloride is obtained by thermal decomposition of the pentachloride, $ReCl_5$, and forms dark red crystals subliming at 500°. It is weakly dissociated in aqueous solution. The tribromide sublimes as a dark green solid when rhenium is heated in bromine vapour.

The following complex salts of tervalent rhenium are known:

$$K_3[ReO(CN)_4];\ Rb[ReCl_4];\ Cs[ReCl_4].$$

The **dioxide,** ReO_2, $2H_2O$, is a black solid obtained by hydrolysis of potassium rhenichloride, $K_2[ReCl_6]$, or by reduction of potassium per-rhenate in acid solution by zinc. On moderate heating it yields the anhydrous oxide, but at 1000° decomposes thus (cf. MnO_2):

$$7ReO_2 = 3Re + 2Re_2O_7.$$

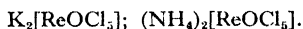
When fused with caustic soda in absence of air, it yields brown insoluble sodium rhenite, Na_2ReO_3, which dissolves in HCl to give a green solution of $H_2[ReCl_6]$. With hydrogen peroxide, ReO_2 yields per-rhenic acid, $HReO_4$ (cf. MnO_2 which decomposes H_2O_2 catalytically).

Rhenium tetrachloride, $ReCl_4$ is said to form (Briscoe, 1931) as a black volatile solid when rhenium is heated in chlorine. It is represented in the green rhenichlorides, $M_2^{\cdot}[ReCl_6]$, whose alkali salts are soluble, those of Ag^+, Hg^+ and Tl^+ being insoluble. The potassium salt, K_2ReCl_6 is obtained by heating $KReO_4$ with concentrated HCl and KI, or by passing chlorine over a mixture of rhenium and potassium chloride (K_2OsCl_6 is similarly produced).

Complex alkali bromides and iodides of the same type are known.

Rhenium disulphide, ReS_2, is a black solid obtained by thermal decomposition of the heptasulphide, Re_2S_7, or from its elements.

Rhenium pentachloride, $ReCl_5$, is a dark brown solid produced from its elements at 500°. It sublimes, and on heating in nitrogen yields $ReCl_3$ and chlorine. With oxygen it forms oxychlorides, $ReOCl_4$ and ReO_3Cl, and with aqueous NaOH forms hydrated ReO_2 and sodium per-rhenate $NaReO_4$ (Geilmann, 1933). The instability of the quinquivalent state is evident here. Green complex salts containing quinquivalent rhenium are known:

$$K_2[ReOCl_5];\quad (NH_4)_2[ReOCl_5].$$

The red **trioxide,** ReO_3, isomorphous with WO_3, is obtained by prolonged heating at 300° of a mixture of ReO_2 and Re_2O_7. Fusion with NaOH yields unstable green sodium rhenate, Na_2ReO_4, and rhenite, Na_2ReO_3. Rhenate solution is unstable even when strongly alkaline.

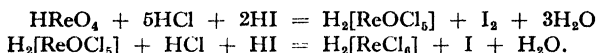
Rhenium hexafluoride, ReF_6 (M.P. 18·5°, B.P. 47·6°) has been prepared from its elements, and gives rise to the solid oxyfluorides, $ReOF_4$ and ReO_2F_2. The compounds $ReOCl_4$ and $K_2[ReOCl_6]$ are known, but $ReCl_6$ is not known.

Rhenium heptoxide, Re_2O_7, formed by direct oxidation of the metal, is remarkably stable (cf. Mn_2O_7 and Cl_2O_7). The white deliquescent solid sublimes above 220°, and with water yields colourless and weakly oxidizing per-rhenic acid, $HReO_4$.

This acid can be prepared by the action of hydrogen peroxide on ReO_2, and its salts by fusing lower oxides with alkali in presence of air. In these reactions, and in the stability of potassium per-rhenate to heat, it offers a remarkable contrast to permanganic acid, which is further heightened by the colourless ReO_4^- ion, and the differences in solubility and crystalline structure of the per-rhenates; $KReO_4$ is isomorphous with $CaWO_4$. Thallous and mercurous per-rhenates are slightly soluble, other metallic salts are soluble. Oxyhalides are known: ReO_3Cl (M.P. 4·5°), ReO_2Cl_3 (M.P. 23°).

The meta-salts, $M \cdot ReO_4$, give rise to yellow meso-per-rhenates: the barium salt, $Ba_3(ReO_5)_2$ is formed from $NaReO_4$ and $Ba(OH)_2$ in presence of aqueous NaOH. With water it yields barium per-rhenate, $Ba(ReO_4)_2$.

In acid solution per-rhenates are reduced to the quinquivalent state by $FeSO_4$ and $Ti_2(SO_4)_3$, while chromous sulphate produces quadrivalent compounds: both reduction stages may be obtained by hydriodic acid, thus (Jezowska, 1934):

$$HReO_4 + 5HCl + 2HI = H_2[ReOCl_5] + I_2 + 3H_2O$$
$$H_2[ReOCl_5] + HCl + HI = H_2[ReCl_6] + I + H_2O.$$

The black **heptasulphide,** Re_2S_7, is produced by the action of hydrogen sulphide on acidified per-rhenate solutions. (Cf. $KMnO_4$ and H_2S). In neutral solution soluble thioper-rhenates, e.g. $KReO_3S$. are said to form.

CHAPTER XII

GROUP VIII

The members of this group occupy a unique position in the periodic table. In each of the three long periods of eighteen, eighteen, and thirty-two elements respectively, the elements of the B are linked to those of the A sub-groups by sets of three, which constitute transitional elements, and are classed together as Group VIII. There are thus nine members of this group,

which are related in the following manner to the adjacent sub-groups:

A					B	
vi	vii	viii			i	ii
Cr	Mn	Fe	Co	Ni	Cu	Zn
Mo	Ma	Ru	Rh	Pd	Ag	Cd
W	Re	Os	Ir	Pt	Au	Hg

The eighth group is thus peculiar in the possession of three members in each series instead of only one; and it would appear that the variation of atomic weights and properties from group to group would on this account be destroyed. Such, however, is not the case, owing to the remarkable fact that the three members in each series have approximately equal atomic weights and physical properties, so that they are analogous to a single element in any other group.

	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
Atomic number .	26	27	28	44	45	46	76	77	78
Atomic weight . .	55·84	58·95	58·69	101·65	102·9	106·7	191·0	193·0	195·2
Density	7·84	8·8	8·8	12	11–12	11·4–12	21·3–24·0	22·4	20·9–21·7
Atomic volume .	7·12	6·70	6·67	8·47	8·9	9·3	8·4	8·6	9·2

The melting-points of these elements are high, that of nickel, about 1452°, being the lowest, and those of iridium and osmium the highest. Iron, with melting-point 1505°, and platinum, with melting-point 1755°, have been vaporized in the electric furnace at a temperature of upwards of 3000°.

The densities of the members of the different sets are related to one another in an approximately similar manner to the atomic weights; so that ruthenium, rhodium, and palladium are intermediate in density as well as in atomic weight between iron, cobalt, and nickel, and the very heavy metals, osmium, iridium, and platinum. With rise of atomic weight there is a diminution of electro-positiveness, as indicated by the potential series; and concomitant with this is a diminution

in chemical activity, in passing, for example, from nickel through palladium to platinum; this being illustrated by the mode of natural occurrence and relative ease of reduction of the metals of the group. Iron seldom occurs, and cobalt and nickel never occur, native, though their oxides are easily reduced; but osmium, iridium, and platinum are always found in the free state.

The mutual relationships of the metals of the eighth group recall those obtaining between copper, silver, and gold in group I B, to which metals they show much resemblance.

Manifestly the members of this group cannot be divided into A and B sub-groups as in the case of other groups; but they may be conveniently studied in the sets into which they naturally fall by reason of their atomic weights and physical properties.

Nevertheless, some vertical relationships are noteworthy. Thus, Fe, Ru, and Os, form isomorphous complex cyanides. Ferrites, and ruthenites, $M^{\cdot}_2RO_3$ exist, and likewise, ferrates, ruthenates, and osmates, $M^{\cdot}_2RO_4$. (Compare also the platinates, $M^{\cdot}_2[Pt(OH)_6]$, isomorphous with stannates, $M^{\cdot}_2[Sn(OH)_6]$.

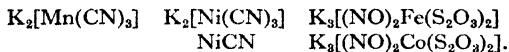
Again, Co, Rh, and Ir, form complex ammines, cyanides, and nitrites, and their sulphates, $R^{\cdot}_2(SO_4)_3$, form true alums.

The remaining elements, Ni, Pd, and Pt, yield complex ammines, cyanides, and nitrites, though nickel is restricted to bivalency and rare examples of univalency.

Since the maximum valency of the members of this family is eight, it is to be expected that these metals will show a large variety of types of compound, as in the case of manganese in which different valencies from one to seven are manifested. This expectation is realized to some extent in the case of iron, less with cobalt and nickel, but more with the remaining members of the group. The higher members of the eighth group possess chemical properties which ally them to gold, to which they approximate in the periodic system. Fairly complete series of oxides and halides are known, acidic

being in most cases more prominent than basic properties.

There is evidence that Group VIII elements, except iridium and osmium, may display univalency, as does manganese, e.g.

$K_2[Mn(CN)_3]$ $K_2[Ni(CN)_3]$ $K_3[(NO)_2Fe(S_2O_3)_2]$
NiCN $K_3[(NO)_2Co(S_2O_3)_2]$.

IRON, COBALT, AND NICKEL

In physical properties cobalt and nickel stand much nearer to one another than they do to iron. This is also true of their chemical relationships, so that in some respects iron stands alone among the elements. Moreover, iron shows a strong likeness to manganese, its neighbour in the seventh group, as well as to chromium. Iron is strongly magnetic, cobalt and nickel are feebly so. All three metals possess high melting-points. Whilst iron rusts in moist air, cobalt and nickel are oxidized only when heated in the air. Red-hot iron decomposes steam, with formation of the oxide Fe_3O_4. Cobalt and nickel form the monoxides under similar circumstances.

The finely divided metals serve as catalysts. Examples are the use of iron in the oxidation of ammonia, and of nickel in the hydrogenation of unsaturated hydrocarbons and fats.

Iron appears to exist in three allotropic forms known respectively as α-, γ-, δ-ferrite. The evidence for this allotropy is the retardation of cooling of the metal from near its melting-point, which is exhibited at certain temperatures, with the accompanying phenomenon of *recalescence.*

These three metals enter into various complex radicles, forming a number of complicated compounds, such as the double cyanides and metallic ammines, but nickel shows less tendency to form these compounds than do iron and cobalt. In this and other respects nickel approximates to copper, whilst cobalt is more nearly related to iron. It must be observed, therefore, that according to properties the order of these elements is Fe, Co, Ni—although the atomic weight of Co is greater than that of Ni. The atomic numbers of these elements (q.v.), however, place them in the order of chemical properties.

CHIEF COMPOUNDS OF IRON, COBALT, AND NICKEL

Typical Oxides.	Fe	Co	Ni
MO ..	FeO $FeCl_2, 4H_2O$; $FeSO_4, 7H_2O$; $FeSO_4, (NH_4)_2SO_4, 6H_2O$	CoO $CoCl_2, 6H_2O$; $CoSO_4, 7H_2O$; $CoSO_4, (NH_4)_2SO_4, 6H_2O$	NiO $NiCl_2, 6H_2O$; $NiSO_4, 7H_2O$; $NiSO_4, (NH_4)_2SO_4, 6H_2O$
M_3O_4 ..	Fe_3O_4	Co_3O_4	Ni_3O_4
M_2O_3 ..	Fe_2O_3 $FeCl_3, 6H_2O$ $Fe_2(SO_4)_3$ various hydrates $Fe_2(SO_4)_3, (NH_4).SO_4, 24H_2O$	Co_2O_3 $(CoCl_3)$ $Co_2(SO_4)_3, 18H_2O$ $Co_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$ $Co_2O(CO_3K)_2$	— — —
MO_2 ..	(FeO_2); $BaFeO_3$	CoO_2	NiO_2
MO_3 ..	(FeO_3); K_2FeO_4	—	—
	$K_4Fe(CN)_6$ $K_3Fe(CN)_6$	$K_4Co(CN)_6$ $K_3Co(CN)_6$ $K_3Co(NO_2)_6$ Complex ammines, e.g. $Cl_3Co(NH_3)_6$	$K_2Ni(CN)_4$ — $K_2CaNi(NO_2)_6$ Ammines, e.g. $NiCl_2, 6NH_3$.

OXIDES OF THE TYPE MO AND THEIR SALTS

Each of these metals forms a monoxide which is basic.

Ferrous oxide, FeO, is a black powder, to which corresponds a white hydroxide, $Fe(OH)_2$, precipitated by alkali from a ferrous solution in absence of air. When a little air is present, a dark-coloured compound of $Fe(OH)_2$ and $Fe(OH)_3$ is produced, which turns to rust-coloured $Fe(OH)_3$ on further exposure. The precipitation of $Fe(OH)_2$ by ammonia is completely prevented by sufficient ammonium chloride. Ferrous compounds are not so oxidizable as the otherwise analogous chromous compounds.

Ferrous salts are white when anhydrous, and pale green or bluish when hydrated. The most important is **ferrous sulphate** or green vitriol, $FeSO_4$, $7H_2O$. In the heptahydrated condition this salt is isomorphous with magnesium and zinc sulphates; crystals having the composition $FeSO_4$, $5H_2O$ have also been obtained which are isomorphous with $CuSO_4$, $5H_2O$, and likewise a salt $FeSO_4$, $4H_2O$ isomorphous with $MnSO_4$, $4H_2O$.

Ferrous ammonium sulphate, or **Mohr's Salt,** $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$, is isomorphous with the corresponding magnesium, zinc, and manganous double salts. Mohr's salt is paler than ferrous sulphate, its colour being that of the hydrated ferrosulphate ion. This salt is said to be more stable than ferrous sulphate, and is therefore preferred for use in volumetric analysis.

Cobaltous oxide, CoO, is a grey powder, and the hydroxide appears to exist in two forms, since when first precipitated it is blue, but becomes rose-red when heated. The hydroxide is oxidized by exposure to air, hydrated Co_3O_4 being produced. It is soluble in hot strong potassium-hydroxide solution, though it can hardly be said to combine with the base, since it crystallizes from the solution on cooling. **Cobaltous salts** are blue, green, or violet when anhydrous, and red or crimson when hydrated. The sulphate forms

several hydrates; the heptahydrate is isomorphous with ferrous and other sulphates, and forms similar double salts.

Nickelous oxide, NiO, is a green crystalline powder obtained from the hydroxide by ignition. When heated at a moderate temperature in air it is converted into a higher oxide, but loses oxygen on further heating, leaving the monoxide, which is stable even at the temperature of the electric furnace. The hydroxide is a green precipitate which, unlike ferrous hydroxide, does not oxidize in air. The **nickelous salts** are usually yellow when anhydrous, and bright green when hydrated. The sulphate crystallizes at atmospheric temperature with seven molecules of water, and is isomorphous with ferrous and other sulphates. The double sulphate, $NiSO_4$, $(NH_4)_2SO_4$, $6H_2O$, is isomorphous with analogous salts containing magnesium, zinc, manganese, iron, or cobalt.

Oxides of the Type M_3O_4

Fe_3O_4 and Co_3O_4 are well known, and Ni_3O_4 ($=2NiO$, NiO_2) also exists. Fe_3O_4, magnetic oxide of iron, is **ferrosoferric oxide,** that is, a compound of ferrous and ferric oxides, FeO, Fe_2O_3. It is black, magnetic, and very stable, since it is obtained by passing steam over red-hot iron, and is the oxide formed when iron is heated in air or oxygen. It may be prepared artificially in a hydrated state by mixing ferrous and ferric solutions in the right proportions and precipitating the mixture with alkali hydroxide. It is not a basic oxide forming salts, but a compound oxide, which may itself be a salt (cf. Pb_3O_4 and Mn_3O_4).

Cobaltocobaltic oxide, Co_3O_4, is obtained by heating cobaltous oxide or nitrate in the air, or in a hydrated condition by the oxidation of moist cobaltous hydroxide; it is analogous to magnetic oxide of iron, and probably has the same constitution; it is the chief constituent of commercial oxide of cobalt.

Oxides of the Type M_2O_3 and their Salts

Ferric oxide, Fe_2O_3, is a dark-red powder, which occurs in nature as red hæmatite, and may be obtained by igniting the hydroxide $Fe(OH)_3$. Ferric hydroxide is formed as a brown precipitate when ammonia is added in excess to a cold solution of a ferric salt. When this precipitate is heated it passes through several stages of dehydration until the anhydrous oxide remains. It is possible for ferric hydroxide to exist in a colloidal condition; this is produced by dissolving ferric hydroxide in ferric chloride solution, or by adding ammonia to ferric chloride as long as the precipitate can be redissolved, and then submitting the liquid to dialysis. Hydrochloric acid formed by hydrolysis of ferric chloride passes through the membrane, leaving almost pure ferric hydroxide in colloidal suspension.

Ferric oxide is a basic oxide, giving rise to the ferric salts, of which the chloride is the best known.

Ferric chloride, $FeCl_3$, occurs in almost black crystalline plates, which are deliquescent and soluble in water, as well as in alcohol, ether, and other organic solvents. It crystallizes from aqueous solution in yellow masses of the composition $FeCl_3, 6H_2O$, and occurs in other hydrated forms. The anhydrous salt begins to volatilize even at 100°, and its vapour density at low temperatures almost corresponds with the formula Fe_2Cl_6. As the temperature rises above 500° the vapour density diminishes. This appears to be due not to dissociation into molecules of $FeCl_3$, but to decomposition into ferrous chloride and chlorine, thus:

$$Fe_2Cl_6 \rightleftharpoons Fe_2Cl_4 + Cl_2.$$

At higher temperatures ferrous chloride forms $FeCl_2$ molecules.

The molecular weight of ferric chloride in organic solvents, however, corresponds with the formula $FeCl_3$. This salt is slowly but completely hydrolyzed by water into colloidal ferric hydroxide and hydrochloric acid. This fact, together with its

solubility in organic solvents, shows ferric chloride to possess some of the properties of a chloranhydride, as well as of a salt. The existence of various double salts, such as $FeCl_3$, $MgCl_2$, H_2O and $FeCl_3$, 2KCl, H_2O, further illustrates this fact.

Ferric sulphate, $Fe_2(SO_4)_3$, is a white powder forming several hydrates, which is easily decomposed, giving rise to basic salts, and is completely hydrolyzed by excess of boiling water. It forms double salts with the sulphates of the alkalis, the well-known iron alums, isomorphous with the similarly constituted aluminium, chromium, and manganese alums. **Ammonium iron alum,** $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $24H_2O$, forms crystals which are light violet when deposited pure from a solution sufficiently acid to prevent hydrolysis. The salt is obtained in a colourless form, however, due to the neutralization of the violet colour by brown, colloidal, ferric hydroxide, when hydrolysis has occurred in the solution from which the crystals separate.* An aqueous solution of the violet salt is brown on account of hydrolysis, but becomes colourless on addition of a little sulphuric acid.

Besides its basic function ferric oxide possesses feebly acidic properties, as indeed would be gathered from the properties of the salts. Ferric oxide combines at high temperatures with certain basic oxides to form ferrites, which are definite, well-crystallized compounds. The best known are calcium ferrite, $CaFe_2O_4$, magnesium ferrite, $MgFe_2O_4$, and zinc ferrite, $ZnFe_2O_4$. Magnetic oxide of iron is ferrous ferrite, $FeFe_2O_4$. In this property ferric oxide resembles alumina, though its acidic functions are much less pronounced, as is shown by the fact that ferric hydroxide is insoluble in alkali hydroxide, while aluminium hydroxide is soluble.

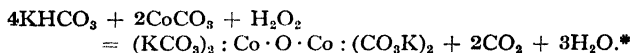
Cobaltic oxide, Co_2O_3. Cobaltous compounds are more easily oxidized than the corresponding nickelous compounds. It has been seen that cobaltous hydroxide is oxidized by air, whilst nickelous hydroxide is stable in air. Ammoniacal cobaltous solutions readily absorb oxygen, forming the cobaltic

* Bonnell and Perman, *Chem. Soc. Trans.* (1921), **119**, 1994.

ammines, a series of complicated compounds which will be studied later. Cobaltic hydroxide is precipitated by means of hypochlorite solution more easily than the nickelic compound. Cobaltous salts generally result when cobaltic oxide is dissolved in acids, but cobaltic acetate is thus produced.

Cobaltic sulphate, $Co_2(SO_4)_3$, may be prepared by the electrolytic oxidation of an acidified solution of the cobaltous salt. It forms blue crystals with $18H_2O$ and is unstable. From it **ammonium cobaltic alum** can be obtained by adding the requisite quantity of ammonium sulphate and crystallizing. This salt forms blue octahedra, which decompose in contact with water, evolving ozonized oxygen.

When a little cobaltous solution is added to a solution of potassium bicarbonate containing hydrogen peroxide, a bright-green liquid results which probably contains a complex **potassium cobaltic carbonate,** formed according to the reaction:

$$4KHCO_3 + 2CoCO_3 + H_2O_2 = (KCO_3)_2 : Co \cdot O \cdot Co : (CO_3K)_2 + 2CO_2 + 3H_2O.^*$$

Nickelic oxide. The oxide obtained when nickel nitrate or chlorate is gently heated, or when nickelous compounds are oxidized in presence of alkali, is not constant in composition, and the existence of Ni_2O_3 has been doubted.† Two hydrates, however, exist, $Ni_2O_3, 2H_2O$ and Ni_2O_3, H_2O, which are believed to be constituted thus:

$$(HO)_2Ni - O - Ni(OH)_2 \text{ and } O = Ni - OH.$$

They dissolve in acids forming nickelous salts, with evolution of oxygen or its equivalent, and on strong ignition form NiO.

Oxides of the Type MO_2

Iron forms a few compounds of the type M_2FeO_3, and definite crystalline nickelites and cobaltites, decomposable by water, such as $BaO, 2NiO_2$, BaO, CoO_2, $BaO, 2CoO_2$,

* Durrant, *Chem. Soc. Trans.* (1905), **87**, 1781.

† Bellucci and Clavari, *Atti R. Accad. Lincei* (1905), **14**, ii, 234.

MgO,CoO_2, are formed by heating the sesquioxides with suitable basic oxides at high temperatures.

The Type MO_3

This type, which is so characteristic of the sixth group, is represented amongst the three metals at present under consideration by the salts of ferric acid, H_2FeO_4, though neither the acid nor its anhydride, FeO_3, is known. **Potassium ferrate,** K_2FeO_4, existing in dark-red crystals, isomorphous with potassium chromate and sulphate, and forming a purple solution, is produced by heating together powdered iron, potassium hydroxide, and nitrate; by passing chlorine into a strong potash solution in which ferric hydroxide is suspended; or by the electrolytic oxidation of iron in a similar solution. The solution of this salt is stable in presence of a small quantity of a mineral salt, but decomposes in presence of acids, alkalis, and reducing agents. The barium salt is more stable, and may be dissolved in dilute acetic acid without decomposition.

THE PLATINUM METALS

The six metals, **ruthenium, rhodium, palladium, osmium, iridium,** and **platinum,** which are associated together in nature, are allied to one another by physical and chemical properties. They are greyish white, very infusible, and show little reactivity, being therefore easily liberated from their compounds. This latter property accounts for their being found in nature in the free state, and is connected with the small atomic volumes of the metals themselves, as has been previously shown. They fall into two groups, with approximately equal atomic weights:

ruthenium, rhodium, palladium,
osmium, iridium, platinum;

and, moreover, the pairs, ruthenium and osmium, rhodium and iridium, palladium and platinum, present natural relationships

in properties. For instance, palladium and platinum both occlude hydrogen, and also form compounds of the type K_2MCl_4; and ruthenium and osmium are alone in forming the tetroxides MO_4, in which the metals are octivalent. In their chemical properties the members of the group show intermediate rather than extreme characters, since their various oxides present prominently neither basic nor acidic qualities. This is quite in accord with their position in the periodic table, between chromium, molybdenum, and tungsten on the one hand, and zinc, cadmium, and mercury on the other. They likewise exhibit some relationships to the members of the iron group, which are manifested chiefly in the complex cyanides and ammines.

The table on p. 476 includes representatives of most of the simple compounds of the platinum metals. Although halides corresponding with several types are well known, comparatively few oxysalts appear to exist. This shows that the basic functions of the oxides of these metals are very feebly developed.

The oxides of the type MO are dark-coloured powders, insoluble in water and most acids. They may be prepared by ignition of the metal in air or oxygen, or by heating the corresponding halide with sodium carbonate. They are decomposed again into their elements by stronger ignition. The hydroxides may sometimes be obtained by decomposing the dichlorides with hot caustic alkali. **Platinous hydroxide,** $PtO, 2H_2O$, for instance, may be prepared in this way. It is difficult, however, to obtain the compound pure, as the chloride is only slowly decomposed, and the hydroxide also shows a tendency to combine with excess of the base. When obtained pure by the action of the theoretical amount of alkali hydroxide on potassium chloroplatinite, K_2PtCl_4, in dilute solution, platinous hydroxide is found to be soluble in hydrochloric and hydrobromic acids, and also in sulphurous acid, but not in other oxyacids. Moreover, it is decomposed by boiling alkali-hydroxide solution into metal and dioxide.

Halides of the type MX_2 exist in the case of most of the

COMPOUNDS OF THE PLATINUM METALS

Typical Oxides	Ru	Rh	Pd	Os	Ir	Pt
MO	— $RuCl_2$	RhO $RhCl_2$ (?)	PdO $PdCl_2$, $PdSO_4$, K_2PdCl_4	OsO $OsCl_2$, $H_4Os(CN)_6$	IrO (?) $IrCl_2$	PtO $PtCl_2$, K_2PtCl_4
M_3O_4	—	Rh_3O_4	—	—	—	Pt_3O_4 (?)
M_2O_3	Ru_2O_3 $RuCl_3$, K_2RuCl_5	Rh_2O_3 $RhCl_3$, K_2RhCl_5, K_3RhCl_6, $Rh_2(SO_4)_3$, and alums	Pd_2O_3 $PdCl_3$, M_2PdCl_5	Os_2O_3 $OsCl_3$, K_3OsCl_6	Ir_2O_3 $IrCl_3$, K_3IrCl_6, $Ir_2(SO_4)_3$, and alums	$Pt_2O_3 \cdot xH_2O$ $PtCl_3$
MO_2	RuO_2 $(RuCl_4)$, K_2RuCl_6, $Ru(SO_4)_2$	RhO_2 —	PdO_2 $(PdCl_4)$, K_2PdCl_6	OsO_2 $OsCl_4$, K_2OsCl_6	IrO_2 $IrCl_4$, K_2IrCl_6, $Ir(SO_4)_2$	PtO_2 $PtCl_4$, K_2PtCl_6, $Pt(SO_4)_2$
MO_3	(RuO_3), K_2RuO_4	RhO_3, Na_2RhO_4	—	(OsO_3), K_2OsO_4 $K_2(OsO_2)Cl_4$	IrO_3 (?)	PtO_3, K_2PtO_4
M_2O_7	(Ru_2O_7), $KRuO_4$	—	—	—	—	—
MO_4	RuO_4	—	—	OsO_4, OsF_8	—	—

Compounds in round brackets ( ) are unknown, but their derivatives exist.

metals, but they do not present truly saline characters. It will be judged from these facts that there are but slight grounds for considering oxides of the type MO to be basic oxides. Indeed acidic functions appear in the tendency to combine with alkalis; and this is further illustrated in the case of the dichlorides of palladium and platinum by the formation of **chloropalladites** and **chloroplatinites** (or platinochlorides); e.g. K_2PdCl_4 and K_2PtCl_4 respectively.

The oxides of the type M_2O_3, and their derivatives, are of little importance. The oxides show less tendency to combine with acids than the monoxides previously considered. **Rhodic nitrate,** $Rh(NO_3)_3$, and **sulphate,** $Rh_2(SO_4)_3$, are known, the latter, as well as $Ir_2(SO_4)_3$, forming a series of alums with the alkali sulphates. The complex chlorides K_3OsCl_6 and K_3IrCl_6 illustrate the acidic functions of the type.

The oxides of the type MO_2, and their derivatives, are the most important compounds of the group. The dioxides of all the six metals are known, and are for the most part stable bodies which are prepared from other compounds by ignition. The corresponding hydroxides, which may be prepared by decomposing the tetrachlorides with alkali hydroxide, possess feebly basic properties; and the sulphates $Ru(SO_4)_2$, $Ir(SO_4)_2$, and $Pt(SO_4)_2$ are known. Moreover, certain of the dioxides form definite compounds with alkalis, **hexahydroxyplatinates** are of the type $M_2Pt(OH)_6$, showing analogy with M_2PtCl_6. Likewise the tetrachlorides combine with the chlorides of the alkali metals to form well-known complex salts containing the acidic ion $(MCl_6)''$. The best-known of these salts are the **chloroplatinates** or **platinichlorides;** for instance, K_2PtCl_6.

The type MO_3 is represented by compounds of ruthenium, rhodium, osmium, and platinum. Ruthenium forms a salt, **potassium ruthenate,** K_2RuO_4, H_2O corresponding with the unknown anhydride RuO_3; this salt, by its mode of preparation and properties, calls to mind potassium manganate, for it is converted by dilute acids into **potassium perruthenate,**

$KRuO_4$, H_2O with separation of a lower oxide. The perruthenate is also formed by the action of chlorine on a solution of the ruthenate; being hydrated it is not isomorphous with the permanganate. **Potassium osmate,** K_2OsO_4, $2H_2O$, crystallizes in octahedra. **Sodium rhodate,** Na_2RhO_4, and **Potassium platinate,** K_2PtO_4, are known.

The tetroxides RuO_4 and OsO_4 are the only known compounds in which four atoms of oxygen are united to a single atom of another element. The nearest approach to this high state of oxidation is seen in permanganic and perchloric anhydrides. Now the acid corresponding with Mn_2O_7, viz. permanganic acid, although unstable, is a powerful acid, judging by the extent of its electrolytic dissociation in aqueous solution; and this is in accordance with the generally observed fact that the presence of oxygen intensifies acidity.

In the case of ruthenium, salts corresponding with the acids H_2RuO_4 and $HRuO_4$ are known, as was mentioned above, although the acids themselves have never been obtained. Since the tetroxide dissolves in water it would be expected to form a strong acid. This, however, is not the case, for the solution does not possess an acid reaction, and does not decompose carbonates. The same is true of the corresponding solution of osmium tetroxide, which is erroneously known as osmic acid. Both these oxides are low-melting, volatile solids, which, when heated, decompose into oxygen and the dioxide. Their solutions are reduced by organic matter with the precipitation of finely-divided metal. On this account a solution of "osmic acid" is used for staining microscopic preparations.

The neutral property of these tetroxides, due to complete absence of hydroxylation in aqueous solution, presents a unique phenomenon. It has been previously observed, however (p. 106, that power of hydroxylation of typical oxides diminishes regularly from the fourth group onwards, and consequently should disappear in the eighth group. In sub-group VII A the analogues of ruthenium and osmium are masurium and

rhenium, and mono-hydroxylation is shown in per-rhenic acid which, like permanganic acid, is monobasic. Therefore the neutral character of these tetroxides is quite in accordance with the requirements of the periodic law, and with the inertness of the oxides of the eighth group. Nevertheless feeble compounds with alkali hydroxides exist, e.g. OsO_4, 2KOH, which are strongly hydrolyzed in aqueous solution.* A volatile **octifluoride,** OsF_8 (B.P. 47·5°) corresponds with OsO_4.

COMPLEX CYANIDES, AMMINES, AND ALLIED COMPOUNDS

Two important classes of compounds formed by members of the eighth group remain to be considered; namely, the **complex cyanides** and the **ammines.** Each of these classes of compounds is characteristic of the eighth group as a whole, as well as of some of its immediate neighbours in the periodic table. They will therefore be studied from the point of view of the group.

The two best-known **complex cyanides** are potassium ferro- and ferri-cyanide, $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. The former is regarded as a compound of 4KCN and $Fe(CN)_2$, and the latter of 3KCN and $Fe(CN)_3$. Whilst, however, the former contains ferrous iron and the latter ferric, the iron cannot in either case be separated by precipitation, as in the case of ordinary ferrous and ferric salts. These compounds are not therefore double salts, like the alums, for instance, which separate more or less into their components in solution, but salts of potassium combined with the complex radicles $^{iv}Fe(CN)_6$, and $^{iii}Fe(CN)_6$ respectively. The acids themselves, $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$, can be obtained by the suitable decomposition of their salts. When, therefore, ferrous and potassium cyanides combine together to form potassium ferrocyanide, a profound change takes place, by which a salt of complex constitution is produced, the iron ceasing to be

* Tschugaev, *Compt. rend.* (1918), **167**, 162.

a basic radicle and becoming a constituent of an acidic complex.

One of the best-known **cobaltammines** is luteocobalt chloride, obtained by the oxidation of ammoniacal cobaltous chloride solution in presence of ammonium chloride. It is therefore a cobaltic derivative, and is represented by the formula $Cl_3Co(NH_3)_6$. Some analogy exists between this compound and potassium cobalticyanide, $K_3Co(CN)_6$, the difference being that whilst $Co(CN)_6$ is a tribasic acidic radicle, $Co(NH_3)_6$ appears to be a triacidic basic radicle.

An account will first be given of the complex cyanides and their allied compounds, and then of the metallic ammines, attention being drawn to such analogies as exist between them.

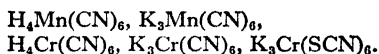
Complex Cyanides

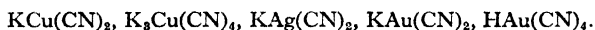
The following are the principal complex cyanides and their allied compounds:

Types	H_2RX_4	H_4RX_6	H_3RX_6	H_2RX_6
Fe		$H_4[Fe(CN)_6]$ $K_4[Fe(CN)_5NO_2]$ $Na_4[Fe(CN)_5AsO_2]$ $Na_4[Fe(SCN)_6]$	$H_3[Fe(CN)_6]$ $K_3[Fe(CN)_5NO_2]$ $Na_3[Fe(CN)_5H_2O]$ $Na_3[Fe(CN)_5NH_3]$ $Na_3[Fe(SCN)_6]$	$H_2[Fe(CN)_5NO]$ $Na_2[Fe(CN)_5H_2O]$ $Na_2[Fe(CN)_5NH_3]$
Ni	$K_2Ni(CN)_4$			
Co		$H_4[Co(CN)_6]$	$H_3[Co(CN)_6]$ $K_3[Co(NO_2)_6]$	
Ru		$H_4[Ru(CN)_6]$		
Rh			$K_3[Rh(CN)_6]$	
Pd	$K_2Pd(CN)_4$ $K_2Pd(NO_2)_2Cl_2$			
Os		$H_4[Os(CN)_6]$		
Ir		$K_4[Ir(CN)_6]$	$H_3[Ir(CN)_6]$ $K_3[Ir(NO_2)_6]$	
Pt	$H_2Pt(CN)_4$ $K_2Pt(SCN)_4$			$K_2Pt(CN)_4Cl_2$ $K_2Pt(SCN)_6$ H_2PtCl_6

Where the acids themselves are known their formulæ are given.

Comparable with the above compounds, manganese and chromium form the following:

$H_4Mn(CN)_6$, $K_3Mn(CN)_6$,
$H_4Cr(CN)_6$, $K_3Cr(CN)_6$, $K_3Cr(SCN)_6$.

And copper, silver, and gold the following:

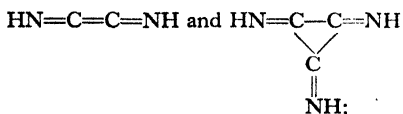
$KCu(CN)_2$, $K_3Cu(CN)_4$, $KAg(CN)_2$, $KAu(CN)_2$, $HAu(CN)_4$.

Likewise the members of sub-group II B, zinc, cadmium, and mercury, form somewhat ill-defined double cyanides.

The complex or double cyanides in the above table present several stages of stability. The least stable are those of nickel and palladium, which, although they can be isolated in the solid state, are decomposed by dilute acids with separation of the simple cyanide. The most stable complex cyanides are those from which the complex acid itself may be isolated. Quite a number of these are known. The formula of the acid itself is given in the table, instead of that of its alkali salt, in cases where the acid is stable and has been isolated.

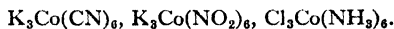
It may again be pointed out, however, that no essential distinction, except in stability, can be drawn between double and complex salts, since all stages of stability exist between those compounds which are decomposed by water or dilute acids, as, for instance, potassium nickelocyanide, and those, such as potassium ferrocyanide, in whose aqueous solutions complex ions exist, and from which the free complex acids themselves can be prepared.

With the recognition of the existence of complex radicles containing cyanogen, arises the question as to their constitution.

It was once customary to regard these salts as derivatives of polymerized hydrocyanic acids,* such as

```
HN=C=C=NH and HN=C—C=NH
                  \ /
                   C
                   ||
                   NH;
```

* Browning, *Chem. Soc. Trans.* (1900), 77, 1233.

but such a view is not consistent with the relationship which obtains between this class of salts and the metallic ammines and analogous compounds. For example, consider the three compounds

$$K_3Co(CN)_6,\ K_3Co(NO_2)_6,\ Cl_3Co(NH_3)_6.$$

It is fair to suppose that the two former bodies are of analogous constitution; and, as was suggested on p. 480, $K_3Co(NO_2)_6$ and $Cl_3Co(NH_3)_6$ are related to one another. Indeed the NH_3 groups in the latter compound may be successively replaced by NO_2 radicles, potassium taking the place of chlorine as the complex cobaltic radicle becomes acidic instead of basic, until finally $K_3Co(NO_2)_6$ results. Moreover, as is shown in the table on p. 480, the complex cyanides themselves can exchange a CN group for another radicle or molecule, such as NO, NO_2, AsO_2, H_2O, or NH_3. Thus the view that the complex cyanides are derivatives of polymerized hydrocyanic acids is inadequate, because it does not admit of substitution of other groups for a CN radicle, nor provide for the classification of these compounds with the large class of metallic ammines to which they are undoubtedly related. The theories which have been put forward regardirg the constitution of the ammines will be considered in the sequel, so that for the present the constitution of the complex cyanides may be left undecided.

Of the compounds tabulated above, a few only of the most important can be considered here.

Potassium ferrocyanide, $K_4Fe(CN)_6,\ 3H_2O$. When potassium cyanide is added to ferrous sulphate solution, the red precipitate first formed dissolves when boiled with excess of the cyanide solution, forming a yellow liquid from which potassium ferrocyanide crystallizes in quadratic pyramids. This salt was at one time prepared by heating iron with potassium carbonate and nitrogenous organic matter, but is now obtained from the cyanides produced in coal-gas manufacture.

Hydroferrocyanic acid, $H_4Fe(CN)_6$, itself separates as a white crystalline solid when hydrochloric acid is added to a concentrated solution of a ferrocyanide. Its ethyl ester possesses the molecular formula $(C_2H_5)_4Fe(CN)_6$.

When potassium ferrocyanide is added to excess of ferric salt, ferric ferrocyanide, or **insoluble Prussian blue,** having the empirical composition $Fe_4[Fe(CN)_6]_3$ is precipitated.

The so-called Turnbull's blue, obtained by precipitating a ferrous salt with ferricyanide solution, is found after washing to be identical with insoluble Prussian blue; thus it appears that ferrous ferricyanide, if at first produced, quickly undergoes intramolecular change into ferric ferrocyanide.

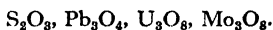
If the ferrocyanide solution is slightly in excess of the iron, the precipitate consists of **soluble Prussian blue,** or hydrated ferric potassium ferrocyanide, $Fe^{\cdots}KFe(CN)_6$, and if ferrous iron is similarly precipitated with a slight excess of ferricyanide solution, the product is soluble Prussian blue identical with the above.

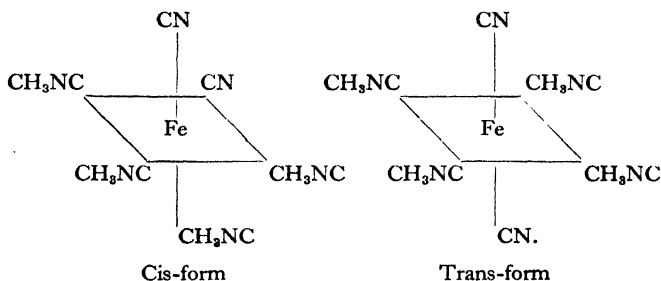
Indeed, it has been shown by Hofmann * that the blue compounds produced by precipitating ferric salts with ferrocyanide, by the oxidation of ferrous ferrocyanide, which is white, or by the reduction of ferric ferricyanide, which exists in solution as a brown compound, all conform to one or other of the formulæ, $Fe^{\cdots}{}_4[Fe(CN)_6]_3$ and $Fe^{\cdots}\ X^{\cdot}[Fe(CN)_6]$, where $X^{\cdot}$=hydrogen or an alkali metal.

The intensely blue colour of these compounds is attributed by Hofmann and Resenscheck (1907), to the presence of both ferrous and ferric atoms within the same molecule.

The dark appearance which precipitated ferrous hydroxide assumes on partial oxidation supports this view, since the dark compound formed is hydrated $Fe_3O_4(=FeO, Fe_2O_3)$. Other examples of highly coloured substances which are compounds of lower and higher oxides of the same element are:

* *Ann.* (1904), **337**, 1; (1905), **340**, 267.

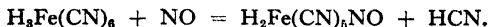
S_2O_3, Pb_3O_4, U_3O_8, Mo_3O_8.

The suggestion that potassium ferrocyanide may exist in isomeric forms has been disproved (Bennett, 1917); nevertheless two isomeric tetramethyl ferrocyanides exist, of empirical constitution, $(CH_3)_4Fe(CN)_6$ (Hartley, 1913). Since methyl groups will not ionize as does potassium, some modification of the potassium ferrocyanide structure is to be expected, and is supported by the production of ammonia and methylamine when the tetramethyl compounds are hydrolyzed, indicating the presence of cyanide and isocyanide groups in the molecule. According to Glasstone (1930), the substance is better formulated as the non-electrolyte, $[Fe(CH_3NC)_4(CN)_2]$, which may exist in the cis- and trans-forms shown below, and in which the CH_3NC molecules are equivalent to ammonia molecules in the ammine structures to be discussed shortly.

Cis-form Trans-form

In $K_4[Fe(CN)_6]$ no isomerism is possible, since each point of the octahedral structure is occupied by CN groups, and the K^+ ions are outwith the complex.

Potassium ferricyanide, $K_3[Fe(CN)_6]$, is a mild oxidizing agent. With H_2O_2 in alkaline solution it is reduced to ferrocyanide, the reverse change occurring in acid solution.

The Nitroprussides.—There remain to be considered compounds of the type H_2RX_6. The red salt $Na_2[Fe(CN)_5NO]$, $2H_2O$, known as sodium nitroprusside, is produced by the action of nitric acid on sodium ferrocyanide. It may be

considered as sodium ferricyanide, in which NaCN has been exchanged for NO. Thus between hydroferricyanic acid and nitric oxide the following reaction takes place:

$$H_3Fe(CN)_6 + NO = H_2Fe(CN)_5NO + HCN.$$

On Sidgwick's view (cf. metallic nitrosyls) the NO molecule here provides three electrons in place of the two removed by $(CN)^-$ when HCN is formed as above. Two of these co-ordinate NO to iron, the odd electron passing to the inner quantum group of the iron atom, so that the ferric iron of the ferricyanide becomes ferrous in the nitroprusside. Did the latter contain ferric iron, analogy with similar compounds leads us to expect a more stable ferrous derivative; that such does not exist, favours the view here given. The NO group in the complex will be positively charged.

This substance is used as a reagent for alkali sulphides, with solutions of which it gives a purple colour. The compound thus produced is very unstable. Its composition may be represented by the formula $Na_4[Fe^{II}(O{=}N{\rightarrow}S)(CN)_5]$.

Hydrogen sulphide itself is not sufficiently ionized in solution to react with nitroprusside.

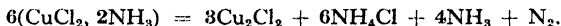
In nitroprussides a (CN)′ group can be exchanged for H_2O or NH_3, as in compounds of other types.

Ammines, or Ammoniacal Compounds of the Metals

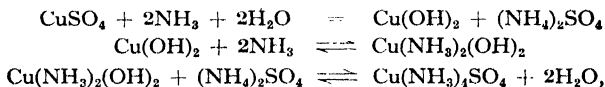
It is well known that when ammonia is added to an aqueous solution of cupric sulphate, the basic sulphate which is at first precipitated dissolves in an excess of ammonia, forming a deep blue liquid. From this liquid long prismatic crystals of cuprammonium sulphate, $CuSO_4$, $4NH_3$, H_2O, can be obtained by adding alcohol to the concentrated solution. Similarly, from cupric chloride crystals of the composition $CuCl_2$, $4NH_3$, H_2O can be produced. Both of these salts lose some ammonia when heated.

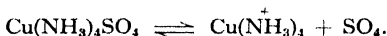
At 150° $CuSO_4$, $4NH_3$, H_2O becomes $CuSO_4$, $2NH_3$, and at 200° $CuSO_4$, NH_3.

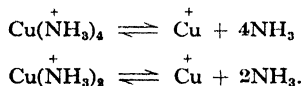
$CuCl_2, 4NH_3, 2H_2O$, which is deep blue, yields the green compound $CuCl_2, 2NH_3$ when moderately heated, and this at higher temperatures breaks up as follows:

$$6(CuCl_2, 2NH_3) = 3Cu_2Cl_2 + 6NH_4Cl + 4NH_3 + N_2.$$

Further, anhydrous $CuCl_2$ absorbs ammonia, forming $CuCl_2, 6NH_3$, whilst anhydrous $CuSO_4$ forms the compound $CuSO_4, 5NH_3$. Cuprous chloride, as well as both cuprous and cupric oxide, also forms compounds with ammonia.

The constitution of these compounds can best be arrived at by a consideration of the properties of their solutions. Dawson and McCrae have shown * that when cupric oxide dissolves in ammonia a soluble base of the composition $Cu(NH_3)_2(OH)_2$ is produced, which undergoes partial electrolytic dissociation into $Cu(NH_3)_2$ and OH ions, and further, that when ammonia is gradually added to a solution of cupric sulphate, the following changes probably take place:

$$\begin{aligned} CuSO_4 + 2NH_3 + 2H_2O &= Cu(OH)_2 + (NH_4)_2SO_4 \\ Cu(OH)_2 + 2NH_3 &\rightleftharpoons Cu(NH_3)_2(OH)_2 \\ Cu(NH_3)_2(OH)_2 + (NH_4)_2SO_4 &\rightleftharpoons Cu(NH_3)_4SO_4 + 2H_2O, \end{aligned}$$

the cuprammonium sulphate thus produced dissociating electrolytically as follows:

$$Cu(NH_3)_4SO_4 \rightleftharpoons Cu(\overset{+}{N}H_3)_4 + SO_4.$$

Probably some of the base $Cu(NH_3)_2(OH)_2$ also exists in the solution, together with its dissociated ions. These compounds easily decompose with the evolution of ammonia, and this takes place in accordance with the following schemes:

$$\begin{aligned} Cu(\overset{+}{N}H_3)_4 &\rightleftharpoons \overset{+}{Cu} + 4NH_3 \\ Cu(\overset{+}{N}H_3)_2 &\rightleftharpoons \overset{+}{Cu} + 2NH_3. \end{aligned}$$

Ammonia is therefore intimately associated with the metal in these compounds; at the same time it appears to take the

* *Chem. Soc. Trans.* (1900), 77, 1239.

place of water of crystallization in the compound $CuSO_4$, $4NH_3$, H_2O.

Compounds of analogous composition are probably produced in the case of cuprous oxide and chloride, as well as with zinc sulphate, cadmium iodide, and nickel sulphate.

Silver chloride forms with ammonia a solution, probably containing the compound $AgNH_3Cl$, and from which crystals of $2AgCl$, $3NH_3$ can be obtained; and the oxide forms a solution containing $AgNH_3OH$, from which the nitride Ag_3N, known as fulminating silver, separates on exposure to air.

Zinc chloride forms several compounds with ammonia, the substance $ZnCl_2NH_3$ being so stable that it may be distilled without decomposition at a red heat.

From analogy to hydrates these compounds may be termed **ammoniates**. They comprise, firstly, the more stable ammines, discussed below, in which NH_3 molecules are definitely associated with the metallic ion, and secondly, the looser and often more highly ammoniated compounds where these molecules form part of the general crystal structure.

Ammoniacal Compounds of the Eighth Group, and of Chromium

A very large number of these ammines are known.

The following are a few typical **cobaltammines** possessing characteristic colours:

Luteocobaltic* chloride, $(NH_3)_6CoCl_3$, is obtained in reddish-yellow prisms when a solution of cobaltous chloride to which ammonium chloride and ammonia have been added is exposed to the oxidizing action of air, bromine, or lead peroxide. If ammonia only is added to cobaltous chloride, hydrochloric acid precipitates from such a solution after atmospheric oxidation **roseocobaltic chloride,** $H_2O(NH_3)_5CoCl_3$. When a solution of this substance in acid is warmed, **purpureocobaltic chloride,** $(NH_3)_5CoCl_3$, is precipitated. The radical NO_2' can replace chlorine from the above compounds.

* *Luteus* = yellow.

Thus from the purpureo salt the following substances may be produced by the action of nitrous acid:

Croceocobaltic* chloride $(NH_3)_5CoCl_2NO_2$.
Xanthocobaltic† chloride $(NH_3)_5CoCl(NO_2)_2$.

Representative examples of cobaltammines and allied bodies are brought together in the following table, in which systematic nomenclature is adopted:

I. *Compounds with a trivalent positive radicle.*

Hexammine cobaltic salts	$[Co(NH_3)_6]X_3$.
Aquopentammine cobaltic salts	$[H_2OCo(NH_3)_5]X_3$.
Diaquotetrammine cobaltic salts	$[(H_2O)_2Co(NH_3)_4]X_3$.
Triaquotriammine cobaltic salts	$[(H_2O)_3Co(NH_3)_3]X_3$.
Tetraquodiammine cobaltic salts	$[(H_2O)_4Co(NH_3)_2]X_3$.

II. *Compounds with a bivalent positive radicle.*

Chloropentammine cobaltic salts	$[ClCo(NH_3)_5]X_2$.
Bromopentammine cobaltic salts	$[BrCo(NH_3)_5]X_2$.
Nitratopentammine cobaltic salts	$[NO_3Co(NH_3)_5]X_2$.
Nitritopentammine cobaltic salts	$[NO_2Co(NH_3)_5]X_2$.
Chloroaquotetrammine cobaltic salts	$[ClH_2OCo(NH_3)_4]X_2$.
Chlorodiaquotriammine cobaltic salts	$[Cl(H_2O)_2Co(NH_3)_3]X_2$.
Chlorotriaquodiammine cobaltic salts	$[Cl(H_2O)_3Co(NH_3)_2]X_2$

III. *Compounds with a univalent positive radicle.*

1·6 Dichlorotetrammine cobaltic salts (praseo ‡)	$[Cl_2Co(NH_3)_4]X$.
1·2 Dichlorotetrammine cobaltic salts (violeo)	$[Cl_2Co(NH_3)_4]X$.
1·6 Dinitritotetrammine cobaltic salts (croceo)	$[(NO_2)_2Co(NH_3)_4]X$.
1·2 Dinitritotetrammine cobaltic salts (flavo §)	$[(NO_2)_2Co(NH_3)_4]X$.
Praseo-diethylenediammine cobaltic salts	$[X_2Co(C_2H_4(NH_2)_2)_2]X$.
Violeo-diethylenediammine cobaltic salts	$[X_2Co(C_2H_4(NH_2)_2)_2]X$.
Carbonatotetrammine cobaltic salts	$[CO_3Co(NH_3)_4]X$.

* κρόκος = saffron.
† ξανθός = the colour of ripe corn.
‡ πράσινος = leek green.
§ *flavus* = golden yellow.

IV. *Compounds with no valency.*

1, 2, 4 Trinitritotriammine cobalt	$[(NO_2)_3Co(NH_3)_3]$.
1, 2, 3 Trinitritotriammine cobalt	$[(NO_2)_3Co(NH_3)_3]$.
Trinitratotriammine cobalt	$[(NO_3)_3Co(NH_3)_3]$.

V. *Compounds with a univalent negative radicle.*

Salts of tetranitritodiammine cobaltic acid $M[(NO_2)_4Co(NH_3)_2]$.

VI. *Compounds with a bivalent negative radicle.*

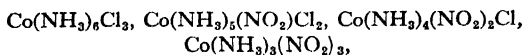
Salts of pentanitritoammine cobaltic acid $M_2[(NO_2)_5Co(NH_3)]$.

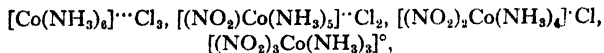
VII. *Compounds with a trivalent negative radicle.*

Salts of hexanitritocobaltic acid (cobaltinitrous acid) $M_3[(NO_2)_6Co]$.
Salts of cobalticyanic acid $M_3[(CN)_6Co]$.

These compounds are all cobaltic derivatives, in which the cobalt atom is normally trivalent. It is to be observed, firstly, that the complex radicle inside the square brackets always consists of a cobalt atom attached to six univalent groups or atoms or their equivalent; secondly, that the exchange of a molecule of ammonia for one of water does not affect the valency of the complex as a whole, so that the group $[H_2OCo(NH_3)_5]$ is trivalent, as well as $[Co(NH_3)_6]$; but that if ammonia is exchanged for acidic atoms or groups, as in $[NO_2Co(NH_3)_5]$, the valency of the whole is diminished to the extent of the valency of the replacing atom or group.

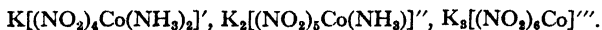
Thus the four compounds, whose empirical formulæ are:

$$Co(NH_3)_6Cl_3,\ Co(NH_3)_5(NO_2)Cl_2,\ Co(NH_3)_4(NO_2)_2Cl,\ Co(NH_3)_3(NO_2)_3,$$

showing a successive diminution in the number of ammonia molecules with the same total number of negative radicles, differ in electric conductivity in equivalent solutions. For at a dilution of 1000 litres the molecular conductivities of the first three salts are 431·6, 246·4, and 98·35 units respectively, whilst that of the fourth salt is almost zero, it being practically a non-electrolyte. The formulæ for these compounds may therefore be written:

$$[Co(NH_3)_6]^{\cdots}Cl_3,\ [(NO_2)Co(NH_3)_5]^{\cdot\cdot}Cl_2,\ [(NO_2)_2Co(NH_3)_4]^{\cdot}Cl,\ [(NO_2)_3Co(NH_3)_3]^{\circ},$$

the radicle within the square brackets constituting a complex basic ion in the first three compounds, and an electrically neutral molecule in the fourth.

It will be observed, however, that the second and third formulæ suggest the possibility of a kind of isomerism; for instance, an alternative to the third compound would be $[Cl(NO_2)Co(NH_3)_4] \cdot NO_2$. Cases of such isomerism have been observed; * the phenomenon is called ionization-metamerism.

From the non-electrolyte $[(NO_2)_3Co(NH_3)_3]$ the three NH_3 molecules may be successively replaced by acidic radicles, so that the valency becomes negative; or, in other words, the molecular complex becomes an acidic instead of a basic radicle. For instance, the following potassium salts may be formulated:

$$K[(NO_2)_4Co(NH_3)_2]', \quad K_2[(NO_2)_5Co(NH_3)]'', \quad K_3[(NO_2)_6Co]'''.$$

The first salt has a molecular conductivity at 1000 litres dilution of 99·29, comparable with 98·35 for $[(NO_2)_2Co(NH_3)_4] \cdot Cl$; the second salt is as yet unknown; the last salt is the familiar potassium cobaltinitrite.

The question now arises as to the relationship of the negative atoms or groups in these compounds to the cobalt atom, since they sometimes form part of the basic radicle, and sometimes constitute acidic radicles. This question is met by the hypothesis that when the negative atom or group is directly attached to the cobalt atom it is not capable of electrolytic dissociation, but forms part of a complex group, whereas when it is attached through a molecule of ammonia it undergoes electrolytic dissociation in solution, and constitutes an acidic radicle.

Thus, in the complex

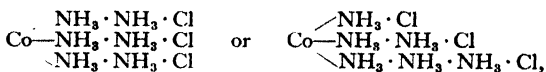
$$Co \langle \begin{matrix} Cl_{(i)} \\ NH_3 \cdot Cl_{(ii)} \end{matrix}$$

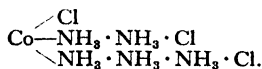
$Cl_{(i)}$ is not ionized in solution, whilst $Cl_{(ii)}$ is ionized. So

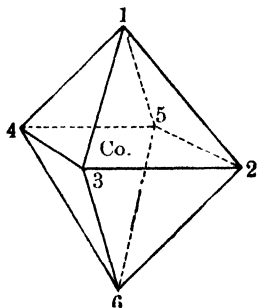
* Werner, *Ber.* (1907), 40, 34.

according to this view, the salts of cobaltammine bases may be regarded as substituted ammonium salts.

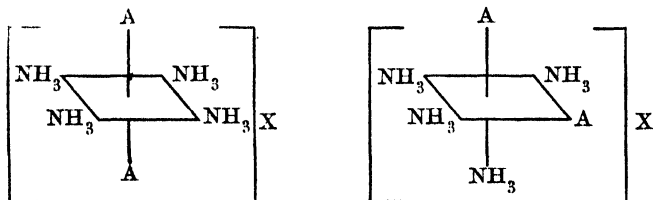
The valency of the cobalt atom remains, however, to be decided. It is possible to represent the constitution of, say, $[Co(NH_3)_6]Cl_3$ in such a manner as to show the cobalt to be trivalent, as by the formulæ:

$$Co\begin{cases} NH_3 \cdot NH_3 \cdot Cl \\ NH_3 \cdot NH_3 \cdot Cl \\ NH_3 \cdot NH_3 \cdot Cl \end{cases} \quad \text{or} \quad Co\begin{cases} NH_3 \cdot Cl \\ NH_3 \cdot NH_3 \cdot Cl \\ NH_3 \cdot NH_3 \cdot NH_3 \cdot Cl, \end{cases}$$

and then to represent a chlorine atom entering the basic complex according to the above principle as follows:

$$Co\begin{cases} Cl \\ NH_3 \cdot NH_3 \cdot Cl \\ NH_3 \cdot NH_3 \cdot NH_3 \cdot Cl. \end{cases}$$

This constitutes the theory of Blomstrand and Jörgensen. Werner, however, has shown that this view does not suffice to account for the remarkable properties of some of these compounds, to which attention must now be drawn.

In the third group of compounds in the table three cases of isomerism are quoted, the isomers differing chiefly in the colours of their salts. Thus, compounds of the type $[A_2Co(NH_3)_4]X$ may be green or violet, and are known as praseo- and violeo-cobaltammines respectively. This phenomenon, first observed by Jörgensen, has been attributed by Werner* to stereo-isomerism, that is, to a difference in the relative positions in space of the six groups around the central cobalt atom, which, together with this atom, constitute the basic radicle. According to Werner, these six atoms or groups lie at the six angular points of a regular octahedron, the cobalt atom being in the centre, as above.

* *Ber.* (1907), **40**, 4817.

It will be seen from an inspection of the figure that the positions 1 and 6 are similarly related to the central plane, whilst the positions 2, 3, 4, and 5 are similarly situated with regard to 1 or 6. Supposing, therefore, that position 1 is occupied by one of the two A atoms or radicles within the basic complex in the compound $[A_2Co(NH_3)_4]X$, the second A atom or radicle may be at 2, say, or at 6, and may thus give rise to two stereo-isomers.* The remaining four positions will in each case be occupied by the four ammonia groups.

Thus Werner represents the isomerism of these compounds in the following way:

This stereo-chemical theory further requires that with three acidic radicles within the basic complex, two isomers should be known in which the three radicles in question occupy the positions 1, 2, and 4, and 1, 2, and 3 respectively. The neutral compound $[(NO_2)_3Co(NH_3)_3]$ is known in two isomeric forms, and thus further support is given to the theory.

Jörgensen † sought to account for the isomerism of the pairs of salts $[(NO_2)_2Co(NH_3)_4]\cdot X$ and $[Cl_2Co(C_2H_4(NH_2)_2)_2]\cdot X$ by assuming differences in the constitution of the NO_2 radicles, and the arrangement of the ethylene-diamine molecules; but, apart from this, Werner,‡ having established the existence of two isomeric salts of the composition $[Cl_2Co(NH_3)_4]\cdot X$, has justified the stereo-chemical formulæ.

* The A radicles might also be considered situated at 2 and 5, and 2 and 4 respectively; the result would be the same.

† *Zeit. anorg. Chem.* (1897), **14**, 410, and (1899), **19**, 109.

‡ *Ber.* (1907), **40**, 4817.

Nevertheless, Werner has departed from the usual ideas of valency in thus accounting for these compounds. Indeed, he assumes that two kinds of valencies exist—principal valencies and auxiliary valencies. Principal valencies are what are ordinarily understood by units of valency; when they are active the saturation capacities of the atoms exercising them are thereby diminished, and the basic or acidic radicles united by means of them are capable of ionization in solution. Auxiliary valencies unite groups of atoms which can ordinarily exist as independent molecules, and which cannot separately become ions; their existence does not diminish the number of principal valencies of the atoms concerned.

Since water and ammonia molecules attached to the cobalt atom do not diminish the ordinary (tri-) valency of that atom, Werner assumes that these molecules are *co-ordinated* with the cobalt atom by means of auxiliary valencies, and the number of them, generally six, is called the co-ordination number. Moreover, he extends this theory to include double and complex salts and crystallohydrates.*

Finally, the following generalization with regard to the cobaltammines and analogous substances may be given:

The combining power of the basic radicle present in ammines and allied compounds is always found to be equal to the difference between the normal valency of the metal, and the number of acidic radicles already included within the complex group containing the metal.

Ammines and analogous compounds formed by other metals may now be briefly mentioned. Of these, the most closely allied to the above are those of **chromium**, derived from chromic salts, among which are the following:

Aquopentammine chromic salts, e.g. $[H_2O(NH_3)_5Cr]^{\cdots}Cl_3$.
Chloropentammine chromic salts, e.g. $[Cl(NH_3)_5Cr]^{\cdot\cdot}Cl_2$.
Nitritopentammine chromic salts, e.g. $[NO_2(NH_3)_5Cr]^{\cdot\cdot}Cl_2$.
Tetrathiocyanatodiammine chromites, e.g. $K[(SCN)_4(NH_3)_2Cr]'$.

* See *Neure Anschauungen auf dem Gebiete der anorganischen Chemie*, by A. Werner, 1909.

It will be noticed that the same law applies to the formation of these chromic compounds as to the cobaltic ammines; and analogous phenomena of isomerism have also been observed.*

Iridium forms three classes of ammines, derived from iridious chloride, $IrCl_2$, from iridic chloride, $IrCl_4$, and from the trichloride, $IrCl_3$, these latter being analogous to the ammines of cobalt and chromium.

All the remaining metals of the eighth group, with the remarkable exception of iron, form ammines, though only those of platinum need be described. Nickel salts form compounds with ammonia, but they are related to the copper ammoniacal compounds rather than to those of cobalt.

Platinum forms two well-defined series of ammines corresponding with the platinous and platinic salts.

The following series is derived from platinous chloride:

Tetrammine platinous chloride	$[Pt(NH_3)_4]Cl_2$.
Chlorotriammine platinous chloride	$[ClPt(NH_3)_3]Cl$.
Dichlorodiammine platinum (two isomers)	$[Cl_2Pt(NH_3)_2]$.
Potassium trichloroammineplatinite	$K[Cl_3Pt(NH_3)]$.
Potassium (tetra)chloroplatinite	$K_2[Cl_4Pt]$.

And the following from platinic chloride, $PtCl_4$:

		Electric Conductivity.
Hexammine platinic chloride	$[Pt(NH_3)_6]Cl_4$.	522·9
Chloropentammine platinic chloride	$[ClPt(NH_3)_5]Cl_3$.	—
Dichlorotetrammine platinic chloride	$[Cl_2Pt(NH_3)_4]Cl_2$.	228
Trichlorotriammine platinic chloride	$[Cl_3Pt(NH_3)_3]Cl$.	96·75
Tetrachlorodiammine platinum (two isomers)	$[Cl_4Pt(NH_3)_2]$.	approx. 0
Potassium pentachloroammineplatinate	$[Cl_5PtNH_3]K$	108·5
Potassium (hexa)chloroplatinate	$[Cl_6Pt]K_2$.	256

In the first of these series the maximum number of ammonia molecules which can exist within the complex is four, and in the second six. It will be observed that the same law concerning the replacement of ammonia by acidic radicles obtains as with the cobalt ammines.

* Pfeiffer, *Ber.* (1904), **37**, 4255.

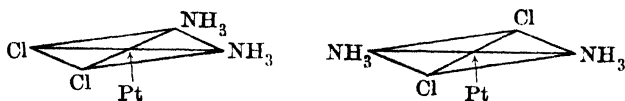
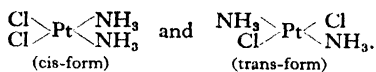
The well-known compounds, the chloroplatinites and chloroplatinates (platino- and platini-chlorides), are regarded as the limiting examples in the two classes of ammine compounds.

Finally, there must be considered the two pairs of isomers which these two classes of platinum ammines afford.

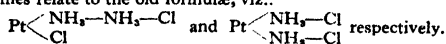
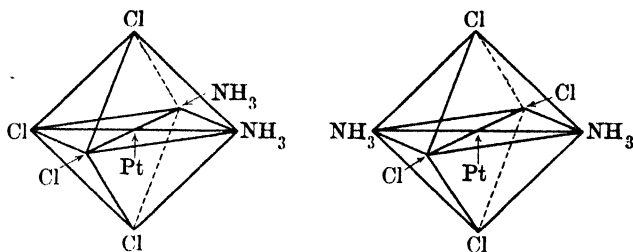
The non-electrolytic, neutral substance $[Cl_2Pt(NH_3)_2]$ contains four groups attached to a central atom in two pairs. It is thus analogous to methylene chloride, CH_2Cl_2. This latter body, however, does not present any phenomenon of isomerism, because the 4 atoms attached to the central carbon atom are equally distributed in space around it, as at the angular points of a regular tetrahedron. If, however, the 4 atoms or groups lay in one plane with the central atom, then isomerism would be possible. The isomerism of the above platinum compounds may be accounted for on this hypothesis, and their stereo-chemical formulæ may be constructed as follows:

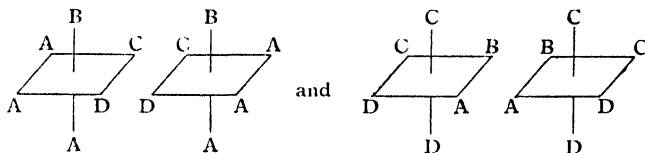
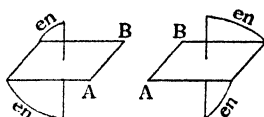
or more simply:

$$\begin{matrix}Cl \\ Cl\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_3 \\ NH_3\end{matrix} \quad \text{and} \quad \begin{matrix}NH_3 \\ Cl\end{matrix}\!>\!Pt\!<\!\begin{matrix}Cl \\ NH_3.\end{matrix}$$

(cis-form) (trans-form)

These two compounds, which have been studied by Werner, and whose geometrical isomerism is appropriately represented by the above formulæ, have been named respectively: chloride of platosemidiammine (cis-form) and chloride of platosammine (trans-form).* If two chlorine atoms are added to each of the above compounds, so that platinic derivatives result, two more isomers are obtained—the tetrachlorodiammine platinum compounds:

* These names relate to the old formulæ, viz.:

$$Pt\!<\!\begin{matrix}NH_3—NH_3—Cl \\ Cl\end{matrix} \quad \text{and} \quad Pt\!<\!\begin{matrix}NH_3—Cl \\ NH_3—Cl\end{matrix} \text{ respectively.}$$

These two bodies are analogous in their isomerism to the two dichlorotetrammine cobalt compounds.

By applying to the above formulæ the principles of "asymmetry" which underlie the formulation of optically active carbon compounds, it is possible to predict the existence of optically active metallic ammines and similar compounds. Thus suppose the six groups or radicles A_3BCD or ABC_2D_2 to surround a nuclear metallic atom; the complex thus produced may exist in two stereo-isomeric forms which are mirror images one of the other, and therefore should possess equal and opposite powers of rotating a beam of polarized light. This is shown in the following schemes:

Werner has realized this optical activity in the case of compounds of cobalt and chromium, where ethylene diamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, symbolized as *en*, displaces CC and DD in the second scheme, thus:

He has also resolved tridipyridyl ferrous bromide $(FeDipyr_3)Br_2$ into optically active components by crystallizing it fractionally with dextro-ammonium tartrate.

Lest it be thought that the optical activity of such isomers is due, not to the nuclear atom, but rather to the organic addenda, it should be noted that the purely inorganic compound

$$[[(OH)_2Co(NH_3)_4]_3Co]Br_6$$

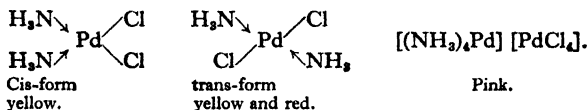
has been resolved into active isomers. The specific rotations given by these compounds sometimes amount to thousands of degrees, far greater than the values obtained from carbon compounds.

Modern chemical theory recognizes Werner's two types of valency in these compounds, and agrees that the principal valency arises from the nuclear atom. It is found, moreover, that when neutral molecules, such as NH_3, enter a complex they do not affect the principal valency, but they themselves furnish the electrons whereby they co-ordinate to the central atom. Thus the nuclear atom is not required to provide the auxiliary valencies of Werner, indeed, its function is receptive only, since it furnishes space for the attachment of the entering molecules. In the cobaltic ammine, $[ClCo(NH_3)_5]Cl_2$, there is room for six atoms or groups disposed octahedrally round the central cobalt atom, and each of these is attached by a bond consisting of two electrons. The sixth member here was originally a negative chloride ion, and its presence in the complex will diminish the total positive charge by one unit, since, in effect, it has returned one electron to the cobalt atom, and is now covalently linked thereto. Two other cobalt electrons are still available, and these are retained by the two chlorine atoms which are united by electrovalencies, i.e. are ionized, and beyond the co-ordination complex which immediately surrounds the cobalt atom. Werner's principal valency of the tervalent cobalt atom is here composite, consisting of one covalency and two electrovalencies. Thus, his formula, $[ClCo(NH_3)_5]^{++}Cl_2^{-}$ is confirmed.

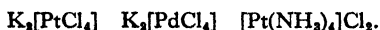
When isomerism produces optical activity, the structures deduced therefrom rest on the very secure basis of the asymmetry of the molecule.

Space-isomerism of the cis- and trans- type is more difficult to establish for apparent isomerism may not be due to similar geometrical plan, but to different structures altogether. Here X-ray analysis is valuable.

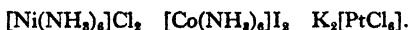
Four compounds exist having the same empirical composition as the diammine of palladous chloride $(NH_3)_2PdCl_2$. Two are yellow and amorphous, two are crystalline, one pink, one red. According to Grünberg (1933), Drew (1932), Mann (1935), and their co-workers, these have the structures:

$H_3N\searrow Pd \swarrow Cl$ / $H_3N\nearrow \ \searrow Cl$	$H_3N\searrow Pd \swarrow Cl$ / $Cl \swarrow \ \nwarrow NH_3$	$[(NH_3)_4Pd]\,[PdCl_4]$.
Cis-form yellow.	trans-form yellow and red.	Pink.

The pink compound is therefore a pallado-chloride of a salt-like structure, while Mann attributes the yellow and red modifications of the same trans-molecules to different crystal structure.

For the most part the arrangement of four atoms or groups round a central atom is tetrahedral, but Werner's co-planar structure has been substantiated in certain 4-covalent compounds of bivalent platinum and palladium, and, following theoretical predictions by Pauling, has been extended to nickel (Sugden, 1932), and to copper (Cox, 1936). By X-ray methods, a planar configuration has been confirmed in the complex ions of

$$K_2[PtCl_4] \quad K_2[PdCl_4] \quad [Pt(NH_3)_4]Cl_2.$$

In certain cases a tetrahedral arrangement seems possible, for optically active compounds of 4-covalent platinum, nickel and copper have been reported.

Similarly, the octahedral grouping, MX_6, is confirmed in

$$[Ni(NH_3)_6]Cl_2 \quad [Co(NH_3)_6]I_2 \quad K_2[PtCl_6].$$

Examples of co-ordination compounds will be found throughout this book: the list below contains some of a purely inorganic type arranged in order of co-ordination numbers (C.N.).

C.N.				
1.	$[Fe(NO)]SO_4$;	$K[Ag(S_2O_3)]$.		
2.	$K[Ag(CN)_2]$;	$K[Cu(CN)_2]$;	$[Ag(NH_3)_2]Cl$.	
3.	$H[HgCl_3]$;	$K_2[Ni(CN)_3]$;	$[Ag(NH_3)_3]Cl$.	
		$K_2[Mn(CN)_3]$		
4.	$[Cu(NH_3)_4]SO_4$;	$K_2[Mn(CN)_4]$;	$[Be(H_2O)_4]SO_4$.	
	$K_3[Cu(CN)_4]$	$K_2[CdI_4]$	$[Be(BeO)_4]SO_4$	
5.	$Cs_3[ZnBr_5]$;	$K_2[BiCl_5]$;	$K[UF_5]$;	$K[ThF_5]$.
6.	$K_3[Sc(CNS)_6]$;	$K_2[GeF_6]$;	$Na_2[ZrCl_6]$;	$Ca[MnCl_6]$.
	$Fe[Fe(CNS)_6]$	$K_2[PbCl_6]$	$K_2[MoCl_5H_2O]$	$K_3[IrCl_6]$.
			$K_2[HfF_6]$	
7.	$NaH_2[Sn(CNS)_7]$;	$(NH_4)_3[SiF_7]$;	$K_2[CbF_7]$;	$K_4[RuCl_7]$.
			$K_2[TaF_7]$	
8.	$K_4[Mo(CN)_8]$;	$K_3H[PbF_8]$;	$K_3[TaF_8]$;	$K_4[Mn(CN)_8]$.
	$K_4[W(CN)_8]$	$[Ca(NH_3)_8]Cl_2$		
9.	$Na_5[ZrF_9]$.			

In general, co-ordination numbers of four and six are most common, and it will be observed that fluorine and $(CN)'$ produce the highest values. The existence of eight- and nine-fold co-ordination has not been satisfactorily explained: presumably the structure in the first case is cubic, but this is uncertain. In some cases the explanation may lie in the crystal lattice, as has been shown with $(NH_4)_3[HfF_7]$ where the structural units are $(NH_4)_2[HfF_6]$ and NH_4F.

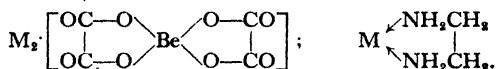
The molybdenum and tungsten compounds $K_4[X(CN)_8]$, are stable, and the free acid, $H_4[W(CN)_8]$ exists. In such a structure, the central atom, X, will possess the same stable number of electrons (its E. A. N.) as the next inert gas, as is the case with Fe in $K_4[Fe(CN)_6]$, thus:

$$[W(CN)_8]^{\equiv} \qquad\qquad [Fe(CN)_6]^{\equiv}$$

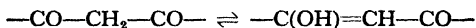
$$W = 74 + 8 + 4 = 86.\ (\text{Rd.}) \qquad Fe = 26 + 6 + 4 = 36.\ (\text{Kr.})$$

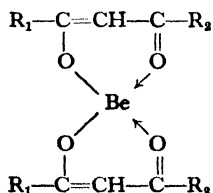
Chelate compounds (Greek *chele*, a crab's claw) are formed when the added molecule or group has two points of

attachment to the centre atom, either by covalency, or co-ordination, or both. Ring structures then arise, as in the complex oxalato-salts or the co-ordination compounds of ethylenediammine:

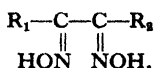
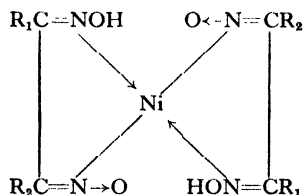
$$M_2\cdot\left[\begin{array}{l}OC—O\diagdown \\ \;| \qquad\quad Be \\ OC—O\diagup\end{array}\begin{array}{l}\diagup O—CO \\ \qquad\quad | \\ \diagdown O—CO\end{array}\right]; \qquad M\begin{array}{l}\swarrow NH_2CH_2 \\ \qquad\quad | \\ \nwarrow NH_2CH_2.\end{array}$$

More than one ring may form should the entering group possess three or even four points of attachment; such groups are tridentate or quadridentate.

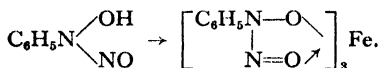
It is a property of certain diketones that they are sufficiently acidic in the enolic form:

$$—CO—CH_2—CO— \rightleftharpoons —C(OH){=}CH—CO—$$

to replace the hydroxyl hydrogen by metals. Apart from the compounds of the alkali metals, these compounds are scarcely salts; in volatility, solubility, and electrical conductivity, they resemble covalent compounds. Werner explained the suppression of saline characteristics by internal co-ordination, as in the beryllium compound of acetylacetone (where R_1 and $R_2 = CH_3$)

$$\begin{array}{c}R_1—C{=}CH—C—R_2 \\ |\qquad\qquad \| \\ O \qquad\qquad O \\ \diagdown \quad \swarrow \\ Be \\ \diagup \quad \nwarrow \\ O \qquad\qquad O \\ |\qquad\qquad \| \\ R_1—C{=}CH—C—R_2\end{array}$$

It was shown by Mills and Gotts (1926) that the valencies round beryllium are arranged tetrahedrally when they found optical activity in the corresponding benzoyl pyruvic acid derivative ($R_1 = C_6H_5$, $R_2 = COOH$).

Particularly valuable are the complexes which nickel forms with substituted glyoximes,

$$\begin{array}{c}R_1—C—C—R_2 \\ \|\quad \| \\ HON \;\; NOH.\end{array}$$

Thus, dimethylglyoxime (R_1 and $R_2 = CH_3$) serves for the estimation of nickel, while, from nickel benzylmethylglyoxime ($R_1 = CH_3$, $R_2 = C_6H_5CH_2$), Sugden (1932) obtained two diamagnetic, cis- and trans-isomers, the nickel valencies being in planar distribution. The trans-structure is shown below, orientation of the structure to bring similar groupings opposite each other will give the cis-form.

Ferric iron may be estimated by the insoluble compound it forms with nitrosophenylhydroxylamine (" cupferron "),

$$C_6H_5N\begin{matrix}\diagup OH\\ \diagdown NO\end{matrix} \rightarrow \left[\begin{matrix}C_6H_5N\!-\!O\diagdown\\ \quad\;\; | \qquad\quad \\ \quad N\!=\!O\nearrow\end{matrix}\right]_3 Fe.$$

Of similar type are many of the insoluble metallic compounds formed by mordant dyestuffs. When chelate compounds are volatile, or soluble in organic solvents, they may be used to effect separations. They have been used also in the theory of maximum covalency. Thus, with acetylacetone ($= A$), it is found that boron forms a salt, $[BA_2]^+X^-$, whereas aluminium forms AlA_3, from which it is inferred that aluminium may be 6-covalent, but boron is limited to a covalency of four.

It has long been known that some organic acids possessing amino- or hydroxy-groups, e.g. tartaric acid, will prevent iron, aluminium, chromium, copper, &c., from displaying their normal reactions. Presumably chelate salts are formed, due to the presence of a donor atom such as oxygen or nitrogen.

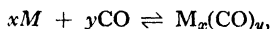
Metallic Carbonyls

Certain salts of elements in Groups I B and VIII form compounds with CO; that one formed by cuprous chloride in

ammoniacal solution, Cu(CO)Cl, has long been used to estimate CO in gaseous mixtures.

Alkali and alkaline-earth elements, and some transition elements, form carbonyls where CO combines directly with the metal. Thus, in liquid ammonia solution, sodium and potassium combine with carbon monoxide to form the coloured, unstable solids, NaCO and KCO, of uncertain structure.

The formation of carbonyls of group VIII elements by direct addition, thus:

$$xM + yCO \rightleftharpoons M_x(CO)_y,$$

is facilitated by high pressure and low temperature.

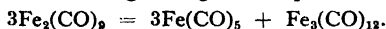
Nickel carbonyl (Mond, 1890), formed as a vapour by passing carbon monoxide over freshly reduced nickel at 30–50°, and atmospheric pressure, is a liquid boiling at 43·2°. It deposits nickel when further heated, and serves for the purification of nickel by the Mond process.

Cobalt carbonyl, $Co_2(CO)_8$, formed at 150° under 40 atmospheres pressure, is orange and crystalline, melting at 51°.

Iron pentacarbonyl, $Fe(CO)_5$, results when the reduced metal is exposed to CO gas for twenty-four hours, and yields yellow crystals at −20°. It is dissociated by light thus:

$$2Fe(CO)_5 \rightleftharpoons Fe_2(CO)_9 + CO;$$

whilst at 100° the following change takes place,

$$3Fe_2(CO)_9 = 3Fe(CO)_5 + Fe_3(CO)_{12}.$$

At 140–150°, $Fe_3(CO)_{12}$ dissociates into metal and CO gas.

The following carbonyls are known: those of group VI are formed from the chlorides in presence of Grignard reagents:

Group VI.		Group VIII.		
$Cr(CO)_6$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	$Ru(CO)_5$
$Mo(CO)_6$	$Fe_2(CO)_9$			$Ru_2(CO)_9$
$W(CO)_6$	$Fe_3(CO)_{12}$	$Co_4(CO)_{12}$		

The monomeric type having one metallic atom are soluble in organic solvents and are volatile; those of group VI A being colourless. Volatility and solubility lessen, and colour

deepens with complexity. They are reducing agents, and decompose with strong acids. When vaporized in air they are explosive.

Nickel carbonyl reacts with alkali only in presence of oxygen to give NiO and CO_2. The more reactive iron pentacarbonyl forms halogen compounds directly, of the type, $[Fe(CO)_4]X_2$, and with alkali, yields a yellow liquid, a carbonyl hydride, M.P. $-70°$, thus:

$$Fe(CO)_5 + Ba(OH)_2 = Fe(CO)_4H_2 + BaCO_3.$$

This reactive substance forms salts with organic bases, and metallic derivatives are known, e.g. $Fe(CO)_4Na_2$, $Fe(CO)_4Cd$, from which the hydride is regenerated by dilute acids. It is a strong reducing agent, and gives with MnO_2 an excellent yield of $[Fe(CO)_4]_3$ (Hieber; Feigl; 1928 onwards). Cobalt carbonyl behaves similarly, yielding $Co(CO)_4H$.

Nitrosylcarbonyls are formed when nitric oxide reacts with iron or cobalt carbonyls. Thus, $Fe(CO)_4$ yields an unstable, red, crystalline compound, $Fe(CO)_2(NO)_2$, M.P. 18·5°, which with iodine gives, $Fe(NO)_2I$. Under pressure, iron pentacarbonyl reacts to give the black tetranitrosyl, $Fe(NO)_4$, while cobalt carbonyl, $Co_2(CO)_8$, at 40°, gives the red liquid, $Co(CO)_3NO$, B.P. 78·6°.

These compounds differ, on the one hand, from nitrosyl compounds of the halanhydride type, e.g. NOCl, and on the other, from the salts formed when nitric oxide is passed into strong acids, e.g. $[NO][ClO_4]$; $[NO][SO_4H]$. These are electrolytes in suitable solvents, furnishing the cation, $[NO]^+$ (Hantzsch, 1930, Angus, 1935). The constitution of " chamber crystals ", nitrosyl sulphuric acid, is probably that given above.

The metallic carbonyls present an interesting problem of valency; and the following types of carbonyls need to be considered:

$$Ni(CO)_4, \quad Co_2(CO)_8, \quad Fe(CO)_5, \quad Mo(CO)_6.$$

According to Sidgwick (*Electronic Theory of Valency*, p. 216) the atoms of nickel and iron, and presumably of cobalt and

molybdenum, should have an Effective Atomic Number (E.A.N.), i.e. the number of electrons in and associated with the atom when in combination, identical with that of the inert gas at the end of the series in which they occur. For Ni, Co, and Fe this number is 36 and for Mo 54. Thus the maximum number of additional electrons which an atom of one of these elements can accommodate in covalent union is the numerical difference between the E.A.N. and the atomic number of the atom.

These numbers are respectively:

For Ni	36 − 28 = 8
,, Co	36 − 27 = 9
,, Fe	36 − 26 = 10
,, Mo	54 − 42 = 12.

Now, if each CO molecule provides two electrons for covalent union with another atom, then the compounds $Ni(CO)_4$, $Fe(CO)_5$, and $Mo(CO)_6$ are at once accounted for. Cobalt carbonyl, as shown by molecular weight determinations is $Co_2(CO)_8$, polymerization furnishing extra electrons to the cobalt atoms to raise their Effective Atomic Number to that of an inert gas. (See Sidgwick, *Proc. Roy. Soc.*, 1934, A, p. 521.)

In $Ni(CO)_4$ and $Mo(CO)_6$ the CO groups are disposed tetrahedrally and octahedrally, respectively, round the metallic atom, being linked thereto thus: $M \leftarrow C \equiv O$.

The structure of NO is uncertain. It is an odd molecule having eleven electrons, one of these being lost to the acid radicle when the salts, $[NO]^+X^-$ are formed. When, however, nitric oxide replaces CO in carbonyls, Sidgwick (*loc. cit.*) suggests that NO provides three electrons towards the E.A.N. of the metal atom, only two of these, however, being used in the link. The E.A.N. of the metal thus equals that of the next inert gas, which, in the examples below, is krypton (36).

$Fe(CO)_2(NO)_2$	$Co(CO)_3NO$
Fe = 26 + 4 + 6 = 36.	Co = 27 + 6 + 3 = 36.

In support of these views, the carbonyls and their nitrosyl derivatives, like the inert gases, are diamagnetic.

CHAPTER XIII

GROUP O

THE NON-VALENT ELEMENTS OF THE HELIUM GROUP

		Atomic number.	Atomic weight.	Boiling-point at atm. press.	Melting-point.	Critical density.
Helium ..	He	2	4·002	−268·5°	cir. −272°	0·065
Neon ..	Ne	10	20·18	−245·8°	−248·6°	0·525
Argon ..	A	18	39·94	−187°	−189·6°	0·5308
Krypton ..	Kr	36	83·7	−151°	−169°	cir. 0·6
Xenon ..	Xe	54	131·3	−109·1°	−140°	0·7661
Radon * ..	Rd	86	222	− 62°	− 71°	—

The discovery of these elements † originated in an observation made by Lord Rayleigh in 1893, that atmospheric nitrogen is about 0·5 per cent heavier than nitrogen obtained chemically. It was at first suggested that this discrepancy was due either to some isolated atoms among the diatomic molecules of chemical nitrogen which would make the gas lighter, or to the presence in the atmospheric gas of some condensed nitrogen molecules, say of N_3, which would account for the increased density.

Experiments were undertaken in conjunction with Sir William Ramsay, who suggested passing the purified atmospheric nitrogen over heated magnesium. Ordinary nitrogen would thus be absorbed, and any portion of the gas differing from the rest might remain. It was found that by this means the density of the gas was perceptibly increased owing to the removal of nitrogen; and finally a small volume of gas remained, the density of which exceeded 19. Rayleigh repeated the experiments of Cavendish, who had passed electric sparks through a mixture of oxygen and atmospheric nitrogen confined over weak potash solution. By this means Cavendish had actually obtained a small bubble of gas which could not be made to combine with oxygen, and Rayleigh confirmed his

* Formerly called Niton (Nt) by Gray and Ramsay.

† *Vide The Discovery of the Rare Gases*, by M. W. Travers, Arnold, 1928.

result. The spectrum of this gas, as well as that of the residue from the magnesium absorption, differed from that of nitrogen or any known gas. Thus it appeared very probable that a new gaseous constituent of the atmosphere had been discovered. Further experiments made this conclusion certain, for it was shown that the proportion of the new gas in air could be increased by diffusion, and by solution in water, in which it is more soluble than nitrogen; and also that nitrogen obtained from sources other than the atmosphere left no residue when submitted to the action of heated magnesium or calcium, or to the sparking process.

The new gas was called "**argon**", on account of its chemical inertness. This property is shown by the following facts. The gas fails to combine with oxygen, the halogens, or red-hot carbon, and also with metals such as magnesium. Attempts to oxidize it by the most powerful oxidizing agents proved fruitless. It enters into the chemical composition of no mineral, vegetable, or animal substance, though occurring in minute quantities in the occluded state in some rare minerals, and in solution in the water of certain springs.

It is now recognized that resistance to atomic union is a distinctive property of argon, and, since chemical union manifests valency, argon is characterized as non-valent.

At temperatures of $-127°$ to $-133°$, and under 40 atmospheres pressure, however, argon and boron trifluoride appear to form a series of compounds A_xBF_3, where $x = 1, 2, 3, 6, 8$ or 16. They have definite melting-points, and are possibly co-ordination complexes of the type $A \rightarrow BF_3$, although in the three highest compounds it seems necessary to assume that polymerization of BF_3 molecules occurs as well.

Further, under pressure, argon, krypton and xenon form hydrates, which are probably due to van der Waals forces.

The question of molecular constitution and atomic weight next arises. Oxygen and nitrogen are known to consist of diatomic and mercury vapour of monatomic molecules, because the data concerning their density can be interpreted by atomic-

weight determinations through chemical union. This method is not available for argon. The density of this gas is 19·95, and its molecular weight, therefore, 39·9; its atomic weight has been determined by means of the following principle:

It is known that the ratio of specific heat at constant pressure to that at constant volume is 1·4 for diatomic, and 1·66 for monatomic gases. This ratio for argon was found by Ramsay to be 1·659. Therefore argon is a monatomic gas, and its atomic weight is 39·9. The atoms of this element thus remain uncombined with one another in the gaseous state.

An attempt to obtain argon from certain minerals, notably from clevéite, resulted in the discovery by Ramsay of another gas, which was found to shine with a pale yellow light when excited electrically in a vacuum-tube. The spectrum of this gas was a brilliant one, and contained a yellow line identical in position with line D_3 observed in the spectrum of the sun's chromosphere during the eclipse of 1868. This line had not previously been found in the spectrum of any terrestrial substance, and the element in the sun giving rise to it had been named " helium " by Lockyer.

In March, 1895, therefore, terrestrial **helium** was discovered. Besides clevéite, the minerals uraninite, bröggerite, and pitchblende yield this gas, together, sometimes, with argon; it has also been obtained from mineral springs. Natural gas from Bow Island, Alberta, Canada, contains 0·33 per cent of helium, and from this source the gas can be obtained on a scale sufficiently large for use in airships. The proposed plant will produce 10,500,000 cubic feet of helium per annum.* Helium is present in minute quantities in the atmosphere; but this gas, like hydrogen, is not dense enough to be retained there permanently, and that lost to space is compensated for by what is evolved from minerals. The density of the gas is 2·001; it is monatomic, the ratio of the specific heats being

* M'Lennan, *Chem. Soc. Trans.* (1920), **117**, 923.

1·652; its atomic weight is therefore 4·002. It belongs to the same category as argon, being reluctant to combine with other elements. The compounds WHe_2 and HgHe or $HgHe_2$ are believed to exist transitorily. Helium is less soluble in water than any other gas. Its boiling-point is 4·5° Abs. This gas probably owes its terrestrial origin to the radioactive processes to be considered in the next chapter.

Consideration of the position of argon and helium in the periodic table led to the conclusion that these were two of a group of inert gases others of which remained to be discovered. In 1898, therefore, Ramsay and Travers made further experiments with residual atmospheric gas.

The gas was compressed in a bulb cooled to −185° by immersion in liquid air. By this means most of the gas was liquefied, and on removal of the bulb from the liquid air its contents were separated into two constituents by rapid exhaustion. These fractions may be called (*a*) and (*b*). The (*a*) fraction, removed as gas, was cooled by immersion in liquid hydrogen, boiling at about −240°. A portion of it solidified, and the remaining gas was found to be helium. The solid proved to be a new element of the argon family, to which the name "**neon**" was given. This element possesses a density of 10·09 and an atomic weight of 20·18, since it is monatomic. It is chemically inert, and gives an orange-red light in a vacuum-tube and a characteristic spectrum.

The fraction (*b*) contained argon, and two new constituents which were named respectively **krypton** and **xenon.** These were separated from one another by fractional distillation, the argon distilling first, krypton next, and xenon last, in accordance with their boiling-points, as given at the head of this chapter. Krypton and xenon resemble argon in the absence of chemical activity, and show characteristic spectra.

These inert and rare gases are used, particularly neon, in the discharge tubes of illuminated signs, and argon is extensively used in gas-filled electric lamps. Sealed capillary tubes of radon are used in the treatment of cancer.

The relative proportions by volume of the minor constituents of the atmosphere are as follows:

Argon	9330	parts per million.
Neon	15·0	,, ,,
Helium	5·0	,, ,,
Krypton	1·0	,, ,,
Xenon	0·1	,, ,,

So minute is the proportion of the last constituent that "it may be said with truth that there is less xenon in the air than there is gold in sea-water" (Ramsay).

Radon, which is isotopic with thoron and actinon, is the emanation of radium. This is a gas, an atom of which is produced from a radium atom by the loss of an α-particle, that is, an atom of helium. Consequently the atomic weight of radon should be $226·0 - 4·0 = 222·0$; the value derived from density determinations is 222. The gas is monatomic, and its physical properties accord with those of the inert gases; it is therefore recognized as the last member of the no-valency group of elements, and is accorded a corresponding place in the periodic system. By its evanescent character, however, it is differentiated from the other elements of the group. The presence in the atmosphere of the emanations of radium and thorium is inferred from the deposition of a radioactive deposit on a negatively charged wire exposed to air, and the observed rate of decay of this deposit.

Radon is isolated by dissolving a radium salt in water, and collecting the evolved gas, which contains also oxygen and hydrogen formed by the decomposition of the water. After exploding these gases and removing the water formed, the radon is condensed in a spiral cooled in liquid air, helium and excess of hydrogen remaining uncondensed. Radon boils at $-62°$ and freezes at $-71°$. The gas is self-luminous on account of the evolved energy of radioactive change; its average life-period is 5–6 days, and by losing an α-particle it gives rise to radium A.

In consequence of this change the spectrum caused by

electric discharge through radon passes after 3–4 days into that of helium. Radon gas, by reason of its radioactive energy, slowly decomposes carbon dioxide, carbon monoxide, ammonia, hydrogen chloride, and water, causes the oxidation of mercury, and turns ordinary white glass violet.

CHAPTER XIV

THE PROBLEM OF THE ORIGIN AND DESTINY OF THE ELEMENTS

Speculations as to the origin and transmutations of matter are as old as human thought. The four elements of the ancients, earth, water, air, and fire, together with the quintessence of Aristotle, were conceived of, not as distinct material species in the modern sense, but as qualities of things which could change with changing circumstances. Thus water, representing the principles of moisture and coldness, could be changed by being heated into air, representing the principles of moisture and heat. The alchemists, who inherited the ideas of the ancient philosophers, attempted to apply them on a material basis; hence there arose the notion of a transmutation, not of properties, but of matter, and the quest for the philosopher's stone which should transmute base metals into gold. So far as the alchemists theorized concerning the nature of this supposed transformation, they believed it to be essentially an exceedingly slow natural process. Thus gold was supposed to grow by degrees, in mines, from common metal. The philosopher's stone, however, would greatly hasten the operations of nature, so as to reward the experimenter with an early crop of the precious metal. The evolutionary idea which underlies these notions appears not to differ in principle from present-day beliefs concerning material transformation; but whilst gold is no longer regarded as the crown of elemental evolution, it is already known that

human agency can influence the rate of material transformation to a limited degree.

Modern ideas of chemical evolution originated with Prout, who in 1815 put forward the suggestion that all the chemical elements are condensations of hydrogen. This suggestion was based upon the belief, which subsequent research dispelled, that the atomic weights determined by chemical analysis, and referred to that of hydrogen as unity, are whole numbers. It will nevertheless be seen in what follows that recent research has revealed in a wonderful way the underlying truth of Prout's hypothesis.

Notwithstanding the abandonment of this belief, the fact remained that interesting relationships between the atomic weights and properties of certain elements could be traced. Döbereiner showed that various "triads" of allied elements exist, the properties and the atomic weight of the central member of a triad being the mean of those of the extreme members. This fact provided the germ of a system of chemical classification of the elements; the beginning of the idea that allied species of elements are to be grouped in genera. This latter conception was much advanced by the law of octaves, and took permanent form in the periodic law.

The question then arose as to the connection between the classification of chemical species and the problem of the origin of such species; or, in other words, whether the periodic law might be taken as evidence of material evolution. Thus the underlying and ultimate question of all chemical science again recurred with increased emphasis; and, although the manner in which the periodic law might be supposed to afford evidence of chemical evolution was not at all clear, it was nevertheless generally accepted as an article of scientific faith, that the ultimate explanation of this great generalization would be found in a theory of the genesis of the elements from a common origin. It must however be stated that to the chief exponent of the periodic law, Mendeléeff, this deduction seemed unwarranted.

In 1887 Crookes gave an account of his researches upon the elements of the rare earths, in which he showed that there exist together in nature a number of bodies which are closely related, and which can only be separated so as to give evidence of distinct chemical identity, by very special and exhaustive means. And, just as the existence of different varieties of the same biological species suggests forcibly their derivation from a common stock, so the closeness of relationship in properties of the metals of the rare earths increases the probability that they are in some manner modifications of a common, original element. To the ultimate element from which by hypothesis all the different kinds of matter are derived, Crookes gave the name " protyle ".

Evidence of Spectra of Stars and Nebulæ

Evidence of inorganic evolution has, however, been sought in a wider field. When the spectroscope was brought into use by Bunsen and Kirchhoff, in 1859, and the significance of the dark lines in the solar spectrum, the so-called Fraunhofer lines, was recognized, the science of cosmic chemistry began. The first work of the new science was the study of the chemistry of the sun; and it was shown that many terrestrial elements are present in our luminary, but that the sun also contains one or two elements which had not then been discovered upon the earth. With the perfecting of experimental methods, investigations spread to the distant stars and nebulæ; until by the accumulation of data, a classification of stars according to their spectra was made possible.

It was thus supposed, at one time, that the evolution of the elements, i.e. their upbuilding from primordial constituents through a process of cooling, could be inferred by comparing together stellar spectra and temperatures. Such a supposition, however, appears to have been premature, for it is not found in modern astrophysics. It is now believed that an evolving star goes first through a process of gravitational contraction

with rise of temperature and corresponding change of spectrum, and then, after reaching a maximum, undergoes a process of cooling on account of radiation, with a reversed change of spectrum; but it is not supposed that changing spectra indicate the actual disruption or synthesis of atoms.

Radioactivity

The evidence afforded by another field of research concerning the breaking down of the elements into simple constituents must now be considered. Following the discovery of Röntgen rays, other substances than glass, which fluoresce without electrical excitement, were examined, in order to discover if they emitted rays. Research upon this subject has brought to light facts of extraordinary interest and significance, which constitute the science of **radioactivity.**

First, it was found by Troost, Becquerel, and Arnold that certain phosphorescent bodies, such as calcium sulphide and hexagonal zinc-blende, emit rays which will act on a photographic plate after passing through aluminium foil 2 mm. thick. The salts of uranium, too, are well known to be fluorescent. Becquerel discovered that this fluorescence is connected with the emission of invisible " rays " which darken a photographic plate through aluminium foil.

There is, however, a fundamental difference between the phosphorescence of calcium sulphide and that of uranium compounds. For whilst the activity of calcium sulphide depends on the previous absorption of light, and therefore diminishes when the compound is kept for some time in the dark, that of uranium preparations is independent of the influence of light, and is not lost even when the material is kept in the dark for a month. This property of " radioactivity " is possessed by various uranium minerals, such as pitchblende, bröggerite, and clevéite, to a greater degree than by uranium salts.

Pitchblende is a complicated mineral containing, besides uranium, barium, bismuth, and thorium, as well as other

components; and the question arose whether the activity of uranium could be concentrated by the fractionation of its salts, or whether this property resided chiefly in some other component of the mineral, since the latter is more radioactive than the uranium salt prepared from it.

The concentration of radioactivity of uranium salt was achieved by Becquerel and Crookes. Becquerel found that on mixing barium chloride with a uranium solution and then precipitating the barium with sulphuric acid, and repeating this operation a number of times, the radioactivity was completely transferred to the barium sulphate, but that the residual inactive uranium regained its activity after eighteen months. This phenomenon suggested the idea that the acquirement of the property of radioactivity is connected in some way with a spontaneous change which uranium undergoes. Crookes separated from uranium salts by fractional crystallization a specially active constituent which he called " uranium X ".

Even more striking results than the above were obtained by the investigation of the other constituents of pitchblende. Thus, in 1898, M. and Mme Curie fractionally crystallized barium halides obtained from pitchblende, and separated therefrom the less soluble halides of **radium**, a new element of the alkaline-earth family, whose radioactivity far exceeds that of uranium.

Similarly, the same observers isolated from the bismuth of the pitchblende another radioactive substance which they named **polonium** and which is identical with Marckwald's radiotellurium.

Shortly afterwards Schmidt and Mme Curie proved that **thorium** and its compounds are radioactive; and in the following year (1899) Debierne obtained another radioactive substance from the thorium of pitchblende, which he named **actinium**.

Most of the facts of radioactivity may be grouped round one or other of the three elements—radium, thorium, and

actinium—and of these three the most interesting and important is radium.

The **chemistry of radium** and its compounds plainly corresponds with the position this element occupies as the highest member of the alkaline-earth group. The metal itself, which has been obtained by Mme Curie and Debierne,* is analogous in properties to barium, and its salts colour the non-luminous gas flame crimson. As would be expected, the chloride, bromide, and sulphate are less soluble than the corresponding barium salts (cf. p. 188). The atomic weight of the element, determined by precipitating its chloride with silver nitrate, is 225·9.

The characteristic phenomena of radium, and of other radioactive substances, are connected with the emission of three kinds of radiation: the α-, β-, and γ-rays, and with the evolution of radioactive gases.

Many chemical changes may be brought about by the action of the rays. Radium salts decompose water in which they are dissolved, and likewise bring about combination between hydrogen and oxygen; they also cause diamonds and other precious stones to phosphoresce and slowly change their colour. Glass tubes containing radium preparations become discoloured; this is probably due to the presence of colloidal metals produced from metallic ions liberated within the glass. Radium preparations confined within glass also effect chemical changes externally, such as the conversion of yellow into red phosphorus, the reduction of mercuric chloride by oxalic acid, the liberation of iodine from iodoform and from iodic acid, and the coagulation of globulin. These changes are brought about by the β- and γ-rays, which possess the power of penetrating glass readily.

The following conclusions regarding the nature of the radium radiations may now be stated provisionally.

The α- and β-radiations consist of minute particles emitted by the radioactive material with immense velocity. They

* *Compt. rend.* (1910), **151**, 523.

are distinguished from each other by (i) their photographic activity, (ii) their power of penetrating layers of air or metal, (iii) their deviability in a strong magnetic field.

The α-**rays** are particles carrying double charges of positive electricity; each particle possesses four times the mass of a hydrogen atom. The velocity of the α-particles is upwards of 10,000 miles a second, and the phosphorescence of hexagonal zinc-blende in Crookes' *spinthariscope* is due to their bombardment. These particles have little photographic activity, or power of penetrating air or aluminium foil; but, owing to the electric charge they carry, a gold-leaf electroscope is rapidly discharged in their presence.

The β-**rays** are also particles. The mass of each is equal to about $\frac{1}{1800}$th that of a hydrogen atom; their velocity varies, but may approach that of light (185,000 miles or 3×10^{10} cm. per second). These particles possess great photographic activity, and are about 100 times as penetrating as the α-rays, so that they will pass through thin aluminium foil, though not through lead 1 cm. thick. In a magnetic field they are deviated a thousand times as much as the α-rays, and in the opposite direction. These properties recall those of the cathode rays, and it is recognized that the β-particles are of the nature of high-velocity cathode rays, or electrons.

The γ-**rays** possess about a hundred times the penetrating power of the β-rays; they will even penetrate a lead shell 1 in. thick. They do not carry an electric charge, and are not deflected in a magnetic field, but, like Röntgen rays, they ionize gases, and so affect an electroscope, and also cause barium platinocyanide to phosphoresce. These rays are not particles, but ethereal vibrations; and they consist of Röntgen rays of very short wave-length and high penetrating power, produced generally but not invariably by the agency of β-rays, just as ordinary Röntgen rays result from the impact of cathode rays on glass.

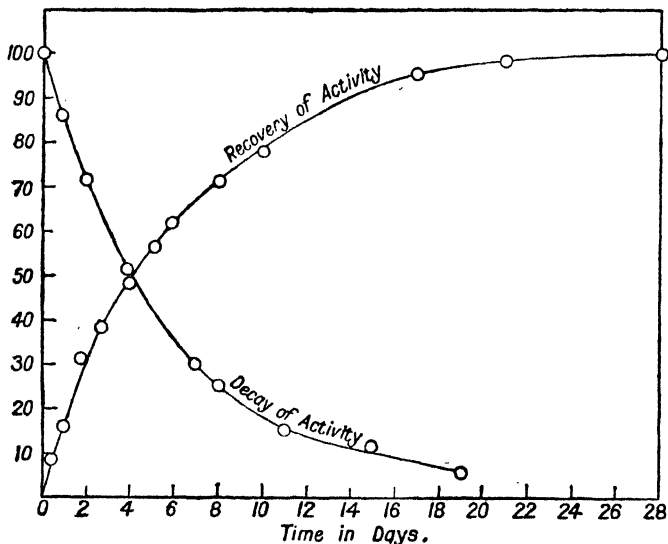
In addition to these different kinds of " rays ", radium,

thorium, and actinium also "*emanate*" radioactive gases of transient activity, which, on account of their physical properties, appear to consist of definitely material particles.

The **radium emanation** may be described. It is best isolated by dissolving a radium salt in water in an evacuated flask. The evolved gases consist, besides the emanation, of water vapour, and of hydrogen and oxygen, produced by the action of the radium on water. After these gases have been eliminated, the emanation can be condensed by liquid air at about $-155°$, and its vaporization with rise of temperature may be observed by the fluorescence of a neighbouring zinc sulphide screen. The passage of the emanation through a glass tube is made visible in the dark by the fluorescence of the glass. Diffusion experiments with the emanation prove it to have a density a little more than 100; it is a monatomic gas, and the last member of the helium group, having an atomic weight of 222. The emanation possesses a characteristic spectrum; it has been recognized definitely as an element, and accordingly has been named *radon*. The thorium and actinium emanations have similar properties, and are also members of the helium family of gases.

When the emanation has been extracted from a radium salt dissolved in water, and the salt is then recovered from solution by evaporation, its radioactivity is found to be feeble compared with that of the emanation. In course of time, however, the salt gains whilst the emanation loses its radioactivity, so that at the end of a month the salt has completely recovered this property, and the emanation has become practically inactive. Moreover, a quantitative study of the phenomena shows that the rates of decay and recovery are equal, so that the sum of the two activities is constant. This is illustrated in the accompanying figure relating to thorium and its emanation, in which radio-activities are plotted against time, so that the reciprocal character of the two curves is made apparent.

The explanation of these phenomena is that the solid radium salt retains within itself the emanation to which the radio-

active effect is chiefly due, so that when the emanation is released from the salt by the process of solution, and from

the solution by evaporation or evacuation, time must elapse for the accumulation of more of it in the solid recovered from solution before the original radioactivity is again reached. Emanation can thus be removed periodically from the radium salt, because it is being continuously generated there. As appears on p. 524, however, there are short-lived radioactive products formed from the emanation which complicate the phenomena, but these do not invalidate the general truth of the above statement.

Radioactive gases have been extracted from deep wells by J. J. Thomson, and from the soil by Elster and Geitel. Radioactivity may apparently be manifested by many common substances, such as lead, wood, and brick, being induced upon this inert matter by contact and by other means. The

emanations of radium and thorium, for instance, can induce radioactivity on paper by contact; and Elster and Geitel found that a platinum wire to which had been given a powerful charge of negative electricity, collected radioactive material from the atmosphere, which, as a solid, could be dissolved from the wire by dilute acid, and deposited on a dish by evaporation of the acid.

So far it has been seen that the substance of radium continuously emits (i) α- and β-particles, together with γ-rays, (ii) a radioactive emanation.

It is necessary now to co-ordinate these facts, and to find some explanation of them.

One explanation alone avails. These phenomena constitute a process of **atomic disintegration** taking place in successive stages, which appear to be beyond human control, but have nevertheless been made known with a fair degree of completeness by the painstaking researches of workers in this field. External temperature conditions have no influence on these incessant changes, for they take place with the same rapidity between $-180°$ and $1600°$. Moreover, they are accompanied by the evolution of heat energy, which was within the atom; so that a mass of radium salt continuously maintains itself at a temperature several degrees above that of surrounding objects.

Exact experiments have shown that 1 gm. of pure radium evolves 133 gramme-calories of heat per hour, or 1,160,000 gramme-calories per annum. Since, as will be seen later, the average life period of radium is 2500 years, 1 gm. of this substance in complete disintegration evolves an amount of heat equal to 2,900,000,000 calories. Compared with all previously known exothermic changes this amount is indeed prodigious. When, for example, 1 gm. of carbon dioxide is produced by the combustion of $\frac{12}{44} = 0{\cdot}273$ gm. of carbon as coal, about 2200 gramme-calories are evolved. Thus the energy of radium is more than a million times the energy of combustion of coal. This fact provides a glimpse at the stores of energy within the

atoms of matter. At present these stores are not within the reach of man; but if future discovery should bring them within reach, the influence that such discovery would have on human life is beyond imagination.

Further particulars may now be given concerning the successive stages of disintegration of radium and similar elements.

It will be convenient to start with the radium and thorium emanations. It has already been observed that a solid disintegration product of some radioactive substance can be collected from the air by a negatively charged platinum wire. Rutherford found that a similar wire exposed to the thorium emanation became radioactive, and that this excited activity could be scraped off the wire or removed from it by hydrochloric acid. It appears, therefore, that the gaseous emanations of radium and thorium give rise to a solid disintegration product, for only a solid could be treated in such a manner.

Rutherford and Soddy believed that helium was also a disintegration product of the radium emanation, and identical with the α-particle; and Ramsay and Soddy showed that when the purified radium emanation is confined in a vacuum tube, its spectrum gives place after three or four days to that of helium. Thus for the first time was witnessed an authentic case of material transmutation; and an explanation was furnished also of the fact that terrestrial helium occurs only in radioactive minerals, whence it is evolved into the air.

The decay of the radium emanation thus consists in the loss of an α-particle which becomes an atom of helium; and the residue, which is solid, constitutes radium A. It has been shown that further changes quickly take place through radium B, radium C, radium D, and radium E to radium F, which is identical with polonium or Marckwald's radiotellurium. By one more radioactive change a permanent, inactive product, radium G, is reached, which has an atomic weight of 206·5,

and is chemically identical with ordinary lead. Thus the history of radium ends in lead; but where does it begin? Is radium itself derived from some other element, known or unknown?

This question may be answered in part by reference to the known facts regarding the rate of disintegration of radium. The amount of emanation produced per unit time depends upon the amount of radium present at the time; and since this amount is constantly diminishing, the amount of emanation produced diminishes accordingly. It has been calculated from actual measurements of the emanation that in 1760 years a given quantity of radium will have reduced itself to one-half; therefore the half-life period of radium is said to be 1760 years.

An alternative and more usual expression to the half-life period is the period of average life. If λ is the fraction of an amount of a radioactive element which disintegrates in unit time, $\frac{1}{\lambda}$ is the average life period. Thus $\frac{1}{2500}$th part of radium disintegrates in a year, therefore the average life period of radium is 2500 years.

Now if all the radium in the earth's crust at the present time were only the remains of an original store of radium, in long past ages this store must have been very great. Considering the known rate of decay, it is estimated that at this rate the amount of radium 26,000 years ago would have been a million times, 52,000 years ago a billion times, 78,000 years ago a trillion times what it is now; and so, many thousands, but not millions of years ago, the earth must all have been radium. This is impossible, and therefore it cannot be believed that the radium now existing is the remains of a store that existed at the beginning. Consequently (if the possible alternative of the synthesis of radium from elements of lower atomic weight is dismissed) it follows that radium is the disintegration product of another element, which necessarily has a higher atomic weight than itself

Now since radium is found in uranium minerals, and the atomic weight of uranium is higher than that of radium, it seemed natural to suppose that uranium is the parent of radium. As will appear later, however, uranium is actually the ancestor rather than the parent of the latter element there being a series of successive disintegrations between the two.

The facts of successive disintegrations of radioactive elements may first be illustrated by the analogy of reservoirs which we owe to Soddy.* Let there be, say, four reservoirs, A, C, B, D, connected in series by pipes of different sizes, leading from the base of each. Then if water flows from A to D through B and C it will reach D at a slower rate than if it flowed direct from A to D. For, suppose reservoirs B, C, and D originally empty; then directly B receives water from A it will begin to deliver it to C at a rate which, at first very small, will increase up to a maximum. This maximum will be reached when the rate of outflow is equal to that of inflow. The rate of outflow cannot exceed that of inflow or there would be no reservoir.

Again, when at an early stage the rate of delivery into C is very small, the rate at which D receives water from C will be infinitesimal; and consequently time must elapse before the presence of water in D is perceived at all. Eventually, however, a condition of equilibrium throughout the whole system will be reached, which depends ultimately on the relative sizes of the pipes; for whilst the rate of flow from each reservoir varies also as the head of water which has accumulated in it, the reservoirs being conveniently supposed of the same sectional area, this accumulation in turn depends upon the pipes delivering water into and from the reservoir. The analogy is thus interpreted. The sizes of the pipes represent the fractions (λ) of radioactive elements which disintegrate in unit time, and these are the reciprocals of the periods of average life. Equilibrium of water in the reservoirs represents

* *The Interpretation of Radium*, 1920 edition, p. 125.

radioactive equilibrium, and the relative amounts of water present in the state of equilibrium stand for the relative quantities of successive products in radioactive equilibrium which are directly proportional to their periods of average life.

Experiments upon the growth of radium from uranium purified from this element were initiated by Soddy and his co-workers in 1904. The formation of radium was detected, but the amount was only about $\frac{1}{1000}$th of what would have appeared if the transition from uranium X, the short-lived successor of uranium, had been direct. This fact suggested the existence of one or more long-lived intermediate bodies; and accordingly such a body was discovered by Boltwood in 1907, and called ionium. Now it follows from the existence of ionium that this body was probably present in the radium-free uranium previously employed. To test the growth of radium actually from uranium it was necessary, therefore, to remove from the uranium not only the radium, but also the ionium from which radium was directly derived, and this being done the growth of radium in the entirely purified uranium would necessarily be even slower than in the previous case; just as in the illustration the arrival in reservoir D of water flowing from A would be slower if reservoirs B and C were empty than if they contained water at the beginning. The growth of radium in uranium purified both from this element and from ionium, was, however, observed by Soddy and Miss Hitchins in 1915, and further confirmed by Soddy in 1919.*
Moreover, from the results obtained the average life-period of ionium has been found to be 100,000 years.

There are now recognized four disintegration products between uranium and radium; and the relative quantities of the successive disintegration products in radioactive equilibrium derivable from a ton of uranium, and their respective periods of average life to which these are directly proportional, are shown in the following table:

* *Phil. Mag.* (1919), 38, 483.

Period of Average Life.	Quantity.
Uranium I, 8,000,000,000 years ..	1,000,000,000 mgm. (= 1 ton)
Uranium X_1, 35·5 days	1/80 mgm.
Uranium X_2, 1·6 min.	1/250,000 mgm.
Uranium II, 3,000,000 years (?) ..	400 gm. (?)
Ionium, 100,000 years	12·5 gm.
Radium, 2500 years	312·5 mgm.
Emanation, 5·6 days	1/500 mgm.
Radium A, 4·3 min.	1/1,000,000 mgm.
Radium B, 38·5 min.	9/1,000,000 mgm.
Radium C, 28·1 min.	7/1,000,000 mgm.
Radium D, 24 years (?)	3 mgm. (?)
Radium, E, 7·5 days	1/400 mgm.
Radium F (Polonium), 202 days	1/14 mgm.

Series of radioactive changes similar to the above have been observed with thorium and actinium. The results may be briefly stated as follows, the radiations lost being placed after each product:

Thorium series.—Thorium (α-rays) → mesothorium I (β-rays) → mesothorium II (β-rays) → radiothorium (α-rays) → thorium X (α-rays) → Th-emanation (α-rays) → thorium A (α-rays) → thorium B (β-rays) → thorium C . . . . . . → end product (lead).

Actinium series.—Actinium (β-rays?) → radioactinium (α-rays) → actinium X (α-rays) → Ac-emanation (α-rays) → actinium A (α-rays) → actinium B (β-rays) → actinium C (α-rays) → actinium D (β-rays) → end product (lead).

As they stand, these schemes are not quite complete, for in each case branch series are known to exist; though, except in the case of the uranium series, they are relatively unimportant.

Radium branch series.—At radium C, whilst 99·97 per cent of the atoms follow the series indicated, 0·03 per cent follow the branch series: Radium C (α-rays) → radium C_2 (β-rays) → end product (lead).

Thorium branch series.—At thorium C 65 per cent of the atoms follow the series: Thorium C (β-rays) → thorium C′ (?) → end product (lead); whilst 35 per cent follow the branch series: Thorium C (α-rays) → thorium D (β-rays) → end product (lead).

Uranium branch series. (Actinium series).—The actinium series is an off-shoot of the uranium series prior to radium. Thus at uranium I or uranium II—probably the latter—8 per cent of the atoms follow the branch series: Uranium Y (β-rays) → eka-tantalum (proto-actinium) (α-rays) → actinium . . . . .

The above disintegration series exhibit about 35 transitional forms of matter, a few of which it is customary to place in the list of elements, whilst the majority do not appear there. For example, in the uranium series, uranium itself, radium, radium emanation (radon), and lead are in the list of the elements; the other members of the series are not. It may be emphasized, moreover, at this stage, that it is evidently quite impossible to find a separate place in the periodic table for each of these transitory forms of matter. What then is to be done with them; or, alternatively, what is to happen to the periodic system?

Now, by the work of Soddy and Fleck, what appears to be an insoluble dilemma has led to a generalization of the greatest importance; and this has prepared the way for new views of the nature of the atoms of matter, which have created a revolution in scientific thought.

To appreciate the generalization which will shortly be stated, the effect upon an atom, as regards the periodic group to which it belongs, of expulsion from it of an α- or a β-particle must be considered. Firstly, it is to be observed that when an α-particle is lost by an atom the atomic weight of the latter is diminished by four units, whilst the loss of a β-particle has no appreciable effect upon the atomic weight.

Thus the relation between radium and its emanation, radon, may be considered. Radium is in periodic Group II, radon in Group O. So by losing an α-particle which carries two + charges an atom has passed backwards by two stages into the periodic group next but one preceding. The loss of a β-particle is the loss of one — charge, and by the same principle this loss should carry the atom forward by one stage into the next periodic group.

The effect of the loss of α- and β-particles in the same series may be tested by tracing the transition from uranium to radium thus:

Uranium (Group VI) loses one α-particle
→ Uranium X_1 (Group IV)
Uranium X_1 (Group IV) loses one β-particle
→ Uranium X_2 (Group V)
Uranium X_2 (Group V) loses one β-particle
→ Uranium II (Group VI)
Uranium II (Group VI) loses one α-particle
→ Ionium (Group IV)
Ionium (Group IV) loses one α-particle
→ Radium (Group II)

So Group II is reached with radium, which is correct. The series may, however, be completed:

Radium (Group II) loses one α-particle
→ Radon (Group O)
Radon (Group O) loses one α-particle
→ Radium A (Group VI)
Radium A (Group VI) loses one α-particle
→ Radium B (Group IV)
Radium B (Group IV) loses one β-particle
→ Radium C (Group V)
Radium C (Group V) loses one β-particle
→ Radium C′ (Group VI)
Radium C′ (Group VI) loses one α-particle
→ Radium D (Group IV)
Radium D (Group IV) loses one β-particle
→ Radium E (Group V)
Radium E (Group V) loses one β-particle
→ Radium F (Polonium) (Group VI)
Radium F (Group VI) loses one α-particle
→ Radium G (lead) (Group IV).

Again, since radium G, which is lead, appears in Group IV, after this long series has been traversed this fact fully justifies the generalization which may now be stated, and is known as:

Soddy's Law

(i) When the atoms of an element expel each an α-particle, the element moves its place in the periodic table two groups backward.

(ii) When the atoms of an element expel each a β-particle, the element moves its place in the periodic table one group forward.

Isotopes.—Now an extraordinary situation arises. The loss of two β-particles electrically neutralizes the loss of one α-particle, and brings an atom back into the same group again. This is seen to be the case above; thus:

In Group IV are:
Uranium X_1 (234), Ionium (230), Radium B (214), Radium D (210), and Radium G (Lead, 206).

It was stated above that a separate place cannot be found in the periodic table for each transitory element; and evidently Group IV cannot provide separate accomodation for each of these new-comers.

Chemically speaking, however, radium B and radium D cannot be distinguished from radium G (lead), and, moreover, uranium X_1 and ionium are chemically identical with thorium.

Thus it appears that the following radioelements are to occupy the same spaces in the periodic table with lead and thorium respectively; and these two latter elements, moreover, occupy the only fourth group positions with which this study is concerned.

Lead ..	.. 207·1	*Thorium* ..	.. 232·4
Radium B	.. 214	Uranium X_1	.. 234
Radium D	.. 210	Ionium ..	.. 230
Radium G	.. 206		

So much as this appears from the study of a single disintegration series. And thus it seems that elements of decidedly different atomic weights are to share a single space in the periodic table because they possess identical chemical properties. Such groups of elements are called by Soddy *isotopes*.*

* I.e. occupying equal positions.

The following is a list of isotopes.

Thallium:—Thorium D, Actinium D, Radium C_2.
Lead:—Radium B, Radium D, Radium G, Thorium B, Thorium D, Actinium B, Actinium D.
Bismuth:—Radium C, Thorium C, Actinium C, Radium E.
Polonium:—Radium A, Thorium A, Actinium A, Thorium C′. Actinium C′, Radium C′.
Radon:—Thorium Emanation, Actinium Emanation.
Radium:—Mesothorium I, Thorium X, Actinium X.
Actinium:—Mesothorium 2.
Thorium:—Uranium X, Ionium, Radiothorium, Radioactinium, Uranium Y.
Uranium X_2 (Brevium):—Uranium Z (Eka-tantalum).
Uranium:—Uranium 2.

Convincing proof of the existence of isotopes lay to hand. Radium G, with atomic weight 206, is said to be lead, i.e. it is isotopic with lead, and is chemically indistinguishable from this metal; yet it cannot be in every way identical with ordinary lead, because this has the atomic weight 207·1. Now the thorium disintegration series also ends with a lead isotope, the atomic weight of which, according to the number of α-particles ejected, starting from thorium, should be $232 - (4 \times 6) = 208$.

To discover whether there exist different kinds of lead which, according to their radio-active origin, possess different atomic weights, evidence has been eagerly sought by actual determinations of the atomic weight of the lead present in radio-active minerals. The result is of extraordinary interest, for lead from thorium-free uranium minerals has been found to have an atomic weight as low as 206·05, and lead from thorium minerals almost free from uranium to have an atomic weight as high as 207·9.

That the atomic weight of an element can vary according to its source is a disturbing discovery; yet the question arises as to why such a discovery has not been made before during the years of accurate atomic weight determinations; for no care has been taken to indicate the source of the elements

experimented upon, as the habitat of a zoological specimen might be indicated. The explanation is that the sources of material for atomic weight determinations have been common and obvious sources, and that apart from contemporary radioactive changes the atomic weight of an element does not vary. This, however, is not to say that the material experimented upon has been homogeneous, but rather that it may have consisted of an unrecognizable but constant mixture of atoms of somewhat different atomic weights, i.e. of isotopes. In the case of lead, for example, it is easy now to suppose that the atomic weight 207·1 results from admixture in the required proportions of isotopes having atomic weights of 206 and 208.

A further question occurs to the mind: since certain isotopes of lead are of radioactive origin, is all lead of such origin? It is not possible to answer this question positively, but it may be pointed out that radioactive origin is origin by disintegration; and allowance must be made also for a constructive evolution of the elements. Nothing is known of the manner of such evolution; yet it is believed that in interstellar space, with absolute zero of temperature, radiation is being changed to matter. On *a priori* grounds there seems as much reason to suppose that lead may be a permanent product of atomic integration as of atomic disintegration. This, however, may be said of any process of atomic integration: that great energy must contribute to it; for the internal stores of atomic energy are enormous.

Separation of Isotopes.—So far as the work of the chemist is concerned the separation of isotopes presents a very difficult problem, because usually no chemical differences are available by which a chemical separation could be achieved. Methods of diffusion, depending on minute differences of density of contiguous atoms or molecules, or other related methods seem to be possible. The very laborious methods of diffusion and fractional distillation have yielded fractions with minute density differences, e.g. in the case of chlorine and mercury

respectively. In the case of hydrogen, however, it has already been noted that the wide disparity between the masses of the isotopes enables a chemical separation to be made. It has been seen also that isotopy is not confined to radioactive elements, but appears generally in the Periodic Classification.

Protoactinium, Pa (eka-tantalum).—Among radioactive elements only those which retain their identity for a sufficient time will be capable of separation chemically. Protoactinium is one such, having a half-life period of 20,000 years, of whose chemistry a little is now known. It is the precursor of actinium in radioactive disintegrations, and was discovered independently by Hahn and Meitner (1917) and Soddy and Cranston (1918).

According to Graue (1934), protoactinium occurs in the residues remaining when radium is extracted from pitchblende. Fusion of these residues with alkali, and subsequent treatment with acid removes first acidic oxides, and then the more basic oxides, leaving a residue richer in protoactinium. This may be dissolved in acid and the protoactinium present co-precipitated with ZrP_2O_7. Further purification isolates the sparingly soluble K_2PaF_7, from which the insoluble hydroxide, and, on ignition of this, the oxide may be obtained.

The lustrous metal is stable to air and may be obtained by thermal decomposition of the chloride on a hot tungsten wire. Its atomic weight is 230·6. As befits the position of protoactinium in Group V A, the oxide Pa_2O_5 is more basic than its predecessors in this sub-group.

At 550°, the oxide reacts with carbonyl chloride to give the crystalline pentachloride, $PaCl_5$, melting at 301°.

Nuclear Transformations.—Two things are characteristic of an element; its atoms possess a definite nuclear charge N, the atomic number, and each atom possesses N electrons external to the nucleus which just neutralize this charge. Radioactive disintegrations and the occurrence of isotopes led to the assumption that the nucleus was composite, containing K + N protons and K electrons, the surplus charge being N.

Now since the mass of an electron is negligible, the mass of an atom is that of its protons, i.e. it is represented by K + N; and since K is independent of N, the mass of an atom is independent of its atomic number, and there appears to be no limit to the number of isotopes, i.e. atoms with the same atomic number, which are possible. Experience shows that the atomic weight of an element is generally rather more than twice its atomic number, that is that the value of K somewhat exceeds that of N; but the ratio of K to N is not constant, and increases somewhat with the value of their sum.

For example:

Element.	Atomic Weight of principal Isotope (K + N).	K	N
C	12	6	6
Cl	35	18	17
As	75	42	33
I	127	74	53
Hg	202	120	80

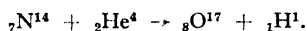
That such a structure will require modification will be evident from what follows.

The spontaneous fracture of an atomic nucleus is the cause of radioactive change or elemental transformation. Such an event has not been brought about by any kind of chemical operation but might conceivably result should the nucleus suffer a direct hit from a particle possessing sufficient energy.

This was accomplished by Sir E. Rutherford in 1919 when he bombarded nitrogen by fast-moving α-particles from radioactive sources. Charged particles having a longer range of travel than the bombarding α-particles were detected by the scintillations they produced on a zinc sulphide screen. They were shown to be protons. The process was photographed by Blackett using the Wilson cloud chamber, and, for the few collisions occurring, the track of the α-particle

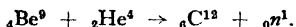
was observed to give place to the track of the lighter proton. It seems that transformation, rather than disintegration occurs, for the α-particle is retained by the nitrogen nucleus which thereupon ejects a proton.

If the symbol for the element be written in association with its nuclear charge and mass-number, as for example, for nitrogen, ${}_7N^{14}$, the above transformation may be written:

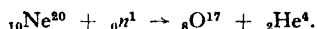
$${}_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1.$$

Besides a proton, an isotope of oxygen of mass 17 has been produced.

Hydrogen nuclei are liberated when other light atoms, e.g. F, B, Na, Mg, are bombarded by α-particles.

The Neutron, *n*.—No protons are liberated when beryllium is bombarded by α-particles, but instead a radiation which can remove protons from paraffin wax (M. and Mme Curie-Joliot). Viewed in the Wilson cloud chamber, the track of the liberated proton is clear, but there is no track connecting the beryllium and the wax. This powerful radiation from beryllium consists of neutrons (Chadwick), having a mass (1·0085) approximately that of the proton itself, but having no charge, and therefore unable to render their paths visible. This nuclear process is formulated:

$${}_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1.$$

Neutrons are also produced from lithium, silicon, and phosphorus by α-particle bombardment.

As bombarding particles, neutrons may also liberate α-particles, as with neon:

$${}_{10}Ne^{20} + {}_0n^1 \rightarrow {}_8O^{17} + {}_2He^4.$$

Other projectiles are protons and deuterons, which may eject neutrons or α-particles from atoms with which they collide: deuterons may also give protons.

By subjecting protons obtained from an electrical discharge tube to a field of the order of 120,000 volts or more, intense

beams of accelerated protons are obtained (Cockcroft and Walton). This work is important, for transformation may now be produced entirely by artificial means.

Induced Radioactivity.—Many of the nuclei produced are unstable, and are radioactive, possessing varying half-life periods. The bombardment of lithium by deuterons is shown thus:

$$_3Li^7 + {}_1H^2 \rightarrow {}_3Li^8 + {}_1H^1,$$

which is followed by

$$Li^8 \rightarrow \beta\text{-particle} + Be^8 \rightarrow 2He^4.$$

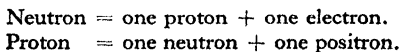
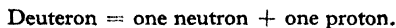
The Positron.—It appears that the earth is continually subjected to a powerful and penetrating radiation, the *cosmic rays*, the source and nature of which are unknown. When examined in a Wilson cloud chamber, under a strong magnetic field, these rays occasionally produce two tracks of opposite curvature due to oppositely charged particles of similar mass. One track is due to the negative electron, the other to its positive counterpart, the positron. Positrons accompanied by electrons, are also produced when some light atoms are subjected to γ-rays: they also appear during some induced radioactive transformations.

The production of positive and negative electrons by γ-rays is of profound significance for it is considered that here is the materialization of energy.

Nuclear transformations, spontaneous and induced, have thus presented us with four entities, the proton, the neutron, the positron and the electron. It is surmised that one of the heavier particles is composite, thus:

Neutron = one proton + one electron.
Proton = one neutron + one positron.

In addition we have:

Deuteron = one neutron + one proton.

These are significant in connection with nuclear structure, for it is not necessary to postulate the existence of free elec-

trons therein. Nuclei may be built of protons and neutrons, the former giving the charge, and the combined masses giving the atomic mass. They may possibly group together as deuterons and helium nuclei, the latter possibly composed of two protons and two neutrons, thus acquiring their mass of four and a charge of two units.

Summary and Conclusion

A few general considerations will bring this account to a close.

So distinctly radioactive an element as uranium has an average life period of 8000 millions of years; and the life periods of elements which have not been observed to be radioactive must be immensely longer than that of uranium. It is consequently impossible to set a limit to the average life period of the commonest terrestrial elements.

Atomic disintegration is accompanied by the disengagement of vast stores of integral energy; and uranium, having the heaviest atoms, possesses the most energy, which it loses in successive stages in its degradation into lead.

These considerations have several far-reaching consequences. Firstly, they have a distinct bearing on the ancient alchemistic problem of transmutation. Since the atom of gold is specifically lighter than that of lead, it is not *a priori* impossible that lead might yield gold by atomic disintegration, and at the same time furnish a large store of heat energy as a by-product. On the other hand, it is *a priori* impossible that silver should be transmuted into gold without the supply of such vast amounts of energy as would render the process economically valueless.

Secondly, the vast stores of energy which are contained within the atoms must have been absorbed during the formation of these atoms from the primal substance; and the disintegration of radioactive elements, which is known to be taking place, must be causing equally vast quantities of energy to be liberated. Consequently it is believed that the internal

heat of the earth, and perhaps the maintenance of solar and stellar temperatures, are to be attributed to the disintegration of radioactive elements. That it may be possible some day for man to utilize the vast stores of sub-atomic energy by causing and controlling atomic disintegration, provides a prospect more revolutionary than any alchemist's dream, but as yet, not within our grasp. According to Rutherford, only about one highly energized α-particle in 100,000 produces transformation of one nitrogen nucleus.

In a former edition of this book it was suggested that the periodic law must constitute a hieroglyphic whose final interpretation would afford a solution of the problem of the origin and destiny of matter. So much advance has now been made towards this goal that the periodic system, modified by the substitution of atomic numbers for atomic weights, has become stereotyped as a completed inventory of the elements. For the additions to our knowledge of the constitution of the atom during recent years have been so wonderful, that whilst it would be unphilosophical to claim absolute or final knowledge concerning this stupendous subject, yet a way has been opened to the springs of what we call the material universe, beyond which it appears to the chemist of to-day that it is hardly possible for him to penetrate.

The origins of the material universe still await solution, and the decision as to how many of the units, proton, neutron, electron, and positron are fundamental, is of first importance. Whether the final analysis will reveal a dualism of particle and electrical property, or will disclose a deeper unity, can only be surmised.

Prout's hypothesis that the atom of hydrogen marks the first step in the evolution of the elements foreshadowed the experimental observation that all atomic nuclei appear to contain protons and their neutral counterpart, neutrons. Atoms synthesized from smaller nuclei, however, do not possess a mass which is the sum of their constituent masses, as Prout supposed, but a small change of mass occurs due to the " pack-

ing" effect. That mass may be lost, e.g. when the helium atom is synthesized from its units, is no doubt repellent to the chemist to whom the conservation of mass has become axiomatic. The finer details of nuclear transformations, however, are in accord with a unified law of conservation, according to which mass and energy are interconvertible. This is no mere speculation, for the genesis of an electron and positron consequent on the annihilation of light energy, as well as the reverse process, can be demonstrated. On the cosmic scale we are even being familiarized with the idea that the sun is losing mass in order to outpour fiery energy unceasingly into space.

The exceedingly minute nucleus is considered to rotate under quantized conditions, and may give rise to γ-rays just as the outer electrons give rise to light in the visible region of the spectrum.

Interwoven with these problems there are others. Why does the wave motion which we call light sometimes behave as if it were little "packets" of energy, or *photons*, recalling Newton's corpuscles, and, on the other hand, why do electrons and beams of free-flying molecules display characteristics of a wave motion?

The atoms of matter are not everlasting; radioactivity is the evidence of their self-destruction. The evolved helium leaves the earth's atmosphere, together with hydrogen, which also is too light to stay here; and it is possible that these terrestrial fragments enter again into the making of new atoms in some far off space. Whether, however, the making and unmaking of matter are processes that repeat themselves as a swinging pendulum repeats its path, is the last question that can be asked; and its answer lies hidden yet beyond the horizon of human knowledge.

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